

## The Effects of In Situ Chemical Oxidation on Aquifer Hydrogeology and Geochemistry

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*Abstract: In situ chemical oxidation is a developing class of remediation technologies in which organic contaminants are degraded in place by powerful oxidants. Although the degradation effectiveness of these oxidants has been demonstrated in numerous laboratory and field-scale tests, the overall effects of the treatment on the aquifer have not been clearly established. A full-scale test of in situ chemical oxidation using potassium permanganate was conducted in a silty-gravel aquifer contaminated by trichloroethylene (TCE) at levels near saturation. Evidence for TCE degradation was found in soil and groundwater samples collected immediately after oxidant injection. Sampling at the field site 10 months after the test was completed revealed significant long-term changes in the hydraulic and geochemical properties of the aquifer. The focus of the presentation will be on the results of the long-term sampling effort as well their implications on the regulatory acceptance of in situ chemical oxidation.*

In situ chemical oxidation is a rapidly developing class of remediation technologies in which oxidants (e.g., potassium permanganate (KMnO<sub>4</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)) are delivered to the subsurface to degrade organic contaminants. In laboratory experiments conducted at Oak Ridge National Laboratory [2], KMnO<sub>4</sub> was generally found to result in more extensive degradation of TCE and tetrachloroethylene (PCE) under a wider range of subsurface conditions when compared to H<sub>2</sub>O<sub>2</sub>. Furthermore, KMnO<sub>4</sub> is inherently more stable than H<sub>2</sub>O<sub>2</sub>, the latter tending to decompose rapidly to H<sub>2</sub>O and O<sub>2</sub> when brought in contact with soil material. The relative stability of KMnO<sub>4</sub> makes it more attractive and effective for applications in which oxidizing power must be maintained over longer time periods, such as when the oxidant needs to be flowed over long distances to treat large volumes of subsurface media.

A field test of in situ chemical oxidation (ISCO) using KMnO<sub>4</sub> was conducted at the X-701B Unit, an area within the U.S. Department of Energy's (DOE) Portsmouth Gaseous Diffusion Plant in Piketon, OH where TCE concentrations in some groundwater wells have been measured at or near saturation [2]. The target aquifer consists of a 5-ft layer of silty gravel bounded above and below by 25 to 30 ft of dense silty clay and bedrock shale, respectively. The ISCO field test was implemented using a pair of parallel horizontal wells that are 90 ft apart and have 200-ft screened sections consisting of 5-in. diameter, high-density polyethylene porous filters (500 mm pore size). Concentrated solutions of KMnO<sub>4</sub> (2 to 4%) were injected through one horizontal well while groundwater was extracted from the adjacent horizontal well, resulting in a distribution of KMnO<sub>4</sub> that clearly showed heterogeneity and preferential flowpaths between the horizontal wells (Fig. 1a). After 3 weeks, oxidant injection was moved from the horizontal well to a vertical well located in the center of the treatment region (74G, Fig. 1). Rapid dispersal of oxidant from the vertical well injection was observed, as shown in Fig. 1b.

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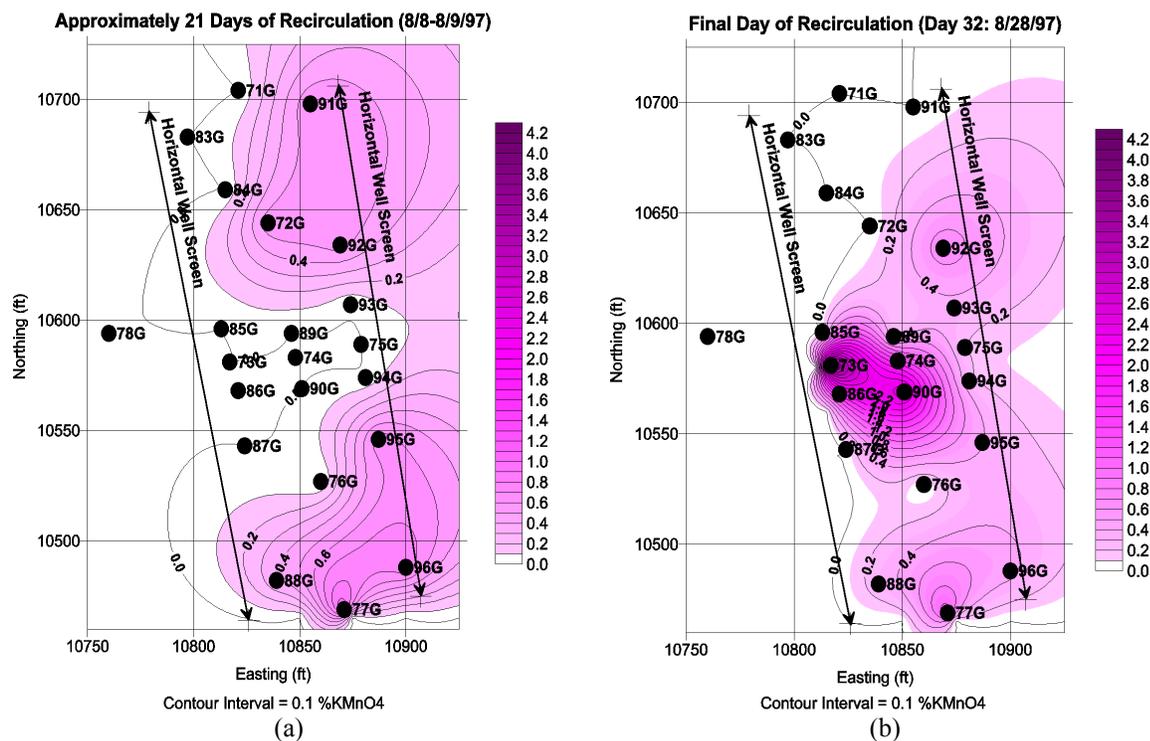


Fig. 1.  $\text{KMnO}_4$  distribution between the X-701B horizontal wells: (a) shows oxidant distribution after 21 days of oxidant injection into the east horizontal well; (b) shows oxidant distribution 32 days after the field test was initiated and 11 days after oxidant injection was moved from the east horizontal well to well 74G.

Overall, whenever  $\text{MnO}_4^-$  was detected in groundwater wells, TCE concentrations dropped to non-detectable or low ppb level. TCE was not detected in soil samples collected adjacent to these monitoring wells, confirming the groundwater monitoring results. More detailed post-treatment TCE levels in groundwater and soil can be found in reference [2].

Sampling at the site ten months after the field test revealed several observations regarding the long-term effects of ISCO using  $\text{KMnO}_4$  on a treated aquifer. Of these effects, the most interesting are reductions in hydraulic conductivity and particulate generation. Hydraulic conductivities in some wells decreased dramatically when compared to measurements made before the oxidant field test (Table 1). The most significant changes occurred in well 74G, which was used for oxidant injection, and well 73G, through which oxidant injection was also attempted but was aborted due to clogging. The reduced hydraulic conductivities are likely due to the precipitation of Mn-oxide, a well-known product of  $\text{MnO}_4^-$  reduction [3]. Total suspended solid levels measured ten months after the field test in  $\text{MnO}_4^-$ -impacted wells were 10 to 100 times higher than background levels (Fig. 2). High suspended solids in wells ~50 and ~400 ft downstream of the field test site (wells 09G and 21G in Fig. 2) indicate that the particles generated by ISCO are mobile and can be advected by ambient groundwater flow out of the treatment region. These results have implications for sites where turbidity downstream of an ISCO-treated region may be an issue. Analysis of the suspended particles by X-ray diffraction and scanning electron microscopy with energy-dispersive X-ray (EDX) show that the particles

are amorphous with Mn as a major component. Other cations such as, K, Fe, Ca, Si were also identified in the EDX spectra. These results suggest that the particles generated in ISCO applications are more complex than the colloidal Mn-oxides observed in laboratory studies conducted using dilute  $MnO_4^-$  solutions [3]. The nature and interaction of these particles with sediments will determine their long-term fate and effects on an ISCO-treated aquifer.

Table 1. Hydraulic conductivities measured in wells in the vicinity of the ISCO field test site.

Well ID	Pre-treatment (ft/day) (March 1997)	Post treatment (ft/day) (June 1998; Trial 1)	Post treatment (ft/day) (June 1998; Trial 2)
73G	39.6	1.0	1.7
74G	182.8	0.6	0.8
76G	24.2	57.7	55.8
77G	411.1	93.6	139.8
78G	65.5	153.8	142.4
80G	31.7	63.7	57.0
81G	60.2	5.5	7.6

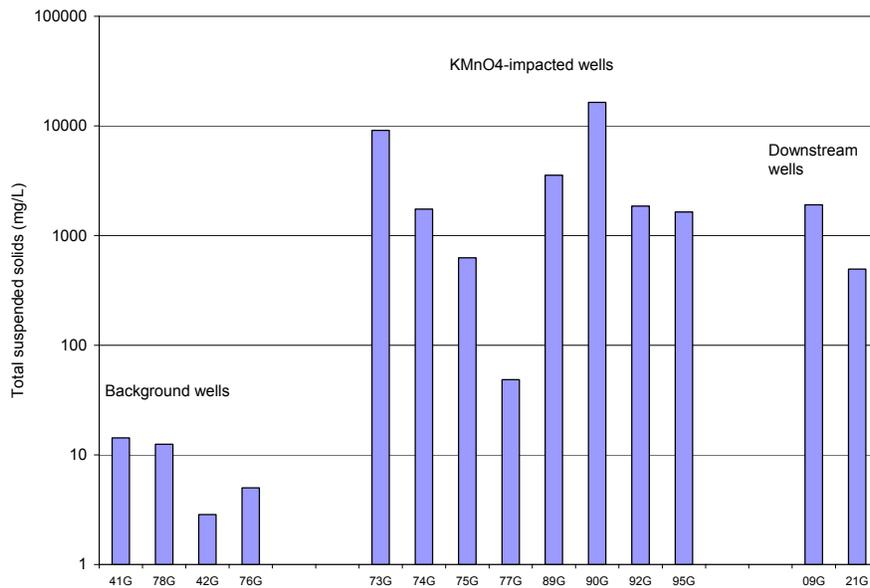


Fig. 2. Total suspended solid levels in wells within the vicinity of the ISCO field test site. Wells 09G and 21G are 50 and 400 ft downstream of the field test site.

### References

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