

Fenton-based Remediation of a Chlorinated Solvent Groundwater Plume Using Segmented Injection Wells – a Field Study

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Abstract

A Fenton-based chemical oxidation pilot test was performed at a former dry cleaning facility in South Florida to evaluate possible full-scale use of this remedial approach for a volatile organic halocarbon (VOH) groundwater plume at the site. Principal contaminants consist of tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (Cis-DCE), trans-1,2-dichloroethene (Trans-DCE), and vinyl chloride (VC). A total of six injection wells (IW) were installed in the apparent source area, where Total VOH concentrations of up to 100,111 ug/l had been detected. Injection wells were spaced no more than 15-feet from one another to achieve overlapping radial influences. Each 4-inch-diameter PVC IW is screened from 6 to 30 feet below land surface (BLS), with 2-foot-thick bentonite seals constructed in the annular space to create separate screened intervals at 6 to 12 feet BLS, 14 to 20 feet BLS, and 22 to 30 feet BLS. The segmented IW allows the use of a specially-designed injector, equipped with K-packers that coincide exactly with the bentonite seals, to direct chemical oxidant to a specific depth interval. Two injection events, separated by six weeks, reduced Total VOH concentrations by 63 percent. PCE and TCE concentrations were reduced by 95 percent and 97 percent, respectively.

Introduction

The work described herein was performed at an abandoned dry cleaner facility that had operated from the early 1960s to 1989. Metcalf & Eddy, Inc. (M&E) conducted a site assessment under the Florida Department of Environmental Protection (FDEP) Dry Cleaner Program, and delineated chlorinated solvent-impacted soil and groundwater. The Dry Cleaner Program has encouraged the evaluation of innovative technologies where appropriate, and *in situ* chemical oxidation was recommended as a possible remedial approach for the groundwater contamination based on the following factors: the source area was well delineated, with dissolved Total VOH concentrations of up to 100,111 ug/l and a contaminant depth profile extending to approximately 30 feet BLS; substantial and apparently ongoing off-site migration of the plume was occurring; the subsurface consists primarily of medium-grain quartz sand, with some silt and limestone fragments; and, the site owner hopes to sell the property as soon as possible.

Site source area samples were then provided to 4 vendors for chemical oxidation bench-scale feasibility testing. Based on the test results, In Situ Oxidative Technologies, Inc. (ISOTEC) was selected for the pilot testing. ISOTEC uses a Fenton-type reaction with a proprietary, chelated iron catalyst and hydrogen peroxide.

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Research within the last three decades demonstrates the effectiveness of Fenton-based processes for oxidation of VOH compounds. Although traditional Fenton's chemistry has existed for over a century, *in situ* applications for site remediation have been limited by difficulties related to maintenance of a low pH, and the poor stability of hydrogen peroxide when introduced into the subsurface. The ISOTEC process features proprietary reagents that allow field propagation of the Fenton's reaction under near neutral pH conditions, while enhancing the mobility of Fe^{2+}/Fe^{3+} ions and improving the stability of hydrogen peroxide. The process works via the generation of hydroxyl radicals as oxidizing agents.

While the oxidizing capability of the process towards VOHs is well established, the success of any *in situ* chemical oxidation process can be limited by the difficulty of bringing the oxidant into contact with the contaminant. In order to more effectively control the application of oxidant, M&E designed and installed segmented IWs. Each 4-inch-diameter PVC IW is screened from 6 to 30 feet BLS, with 2-foot-thick bentonite seals constructed in the annular space to create separate screened intervals at 6 to 12 feet BLS, 14 to 20 feet BLS, and 22 to 30 feet BLS. The segmented IW allows the use of a specially designed injector to direct chemical oxidant to a specific depth interval. Chemical oxidant solution is typically injected through a PVC pipe (injector) inserted down the IW. Special injectors were constructed for this project, featuring K-packers that align exactly with the bentonite seals. The injector is lowered into the IW until the K-packers coincide with the bentonite seals bracketing the desired interval, and chemical oxidant solution is released from the injector through a screen section located between the K-packers. The K-packers and bentonite seals limit vertical migration of the oxidant solution within the IW, and the oxidant emerges from the IW to affect the contaminated aquifer at that specific depth interval. IW depths and locations were decided based on the site assessment data for groundwater, and reflect the approximate horizontal and vertical extent of the core contaminant source area. A total of 6 IW were installed, spaced no more than 15 feet from one another to achieve overlapping radial influences.

Field Procedures

After IW installation, a baseline sampling event was conducted. The 6 IW and 10 selected monitoring wells (MW) were sampled to evaluate upgradient, source area, and downgradient conditions. Samples were analyzed in the field for Turbidity, Ferrous Iron, Dissolved Oxygen, Conductivity, pH, and Temperature. Laboratory analyses were performed for VOH (EPA 601), Ferric Iron, Sulfate, Sulfide, Chloride, Total Organic Carbon, and Total Dissolved Solids.

Following the baseline sampling, chemical oxidation injection # 1 was initiated. Injections were performed at all IWs simultaneously, beginning at the lowest depth interval and moving upward. The injector assembly was installed through a bolt-down well seal, and connected to injection hoses and pumps through a valve assembly. A separate, valved vent opening was provided within the well seal assembly for reaction off-gas release. The injection sequence consisted of introducing a stoichiometric ratio of catalyst to hydrogen peroxide into each injection zone. Flushing with a water buffer was performed between catalyst and peroxide to promote the distribution of the catalyst away from the well, and then following the peroxide to move the peroxide into contact with the distributed catalyst. A total of three injection cycles were performed for each zone of injection during each injection event. The first injection event consisted in total of approximately 2,600 gallons of chelated iron catalyst, and 5,200 gallons of

12 percent hydrogen peroxide. Daily field measurements were obtained from selected wells for Turbidity, Ferrous Iron, Dissolved Oxygen, Conductivity, pH, Temperature, Redox Potential, Hydrogen Peroxide, and Chloride to evaluate radial influence and reaction progress.

Six weeks after the first injection, sampling and analysis identical to the baseline event was performed to obtain an intermediate measure of chemical oxidation performance. A second injection event was then conducted, with procedures and volumes similar to the first injection event. Six weeks after the second injection, a final round of performance sampling was conducted, with sampling and analysis identical to the two previous events.

Results and Conclusions

Table 1 presents Total VOH concentrations for the baseline and two post-injection sampling events. The values shown represent detected concentrations in all 6 IW and 10 MW added together. Post-injection concentrations are also presented as a percentage of baseline concentrations.

Analyte	All Wells 19-Jun-00 (ug/l)	All Wells 1-Aug-00 (ug/l)	All Wells 12-Sep-00 (ug/l)	Injection 1 ÷ Baseline	Injection 2 ÷ Baseline
Vinyl Chloride	18,112	34,856	15,123	192%	84%
Trans-1,2-Dichloroethene	3,566	871	822	24%	23%
Cis-1,2-Dichloroethene	283,199	132,765	110,236	47%	39%
Trichloroethene	14,555	4,246	395	29%	3%
Tetrachloroethene	26,598	5,327	1,268	20%	5%
Other VOH Compounds	174	302	176	174%	101%
<i>Total VOHs</i>	346,204	178,367	128,020	52%	37%

The results support the technical feasibility of the process for site groundwater remediation. Total VOHs were reduced 63% on average, and additional contaminant reduction was achieved with additional injection. TCE and PCE exhibited the best overall reduction, while VC exhibited the poorest. Possible explanations for the lesser reduction of VC are that the oxidation rate for VC may be slower than that for PCE and TCE, and the oxidation of PCE and TCE may be incomplete, resulting in the formation of VC.

In general, VOH decreases correlated well with chloride increases, indicating that oxidation proceeded via a dechlorination pathway. Changes in other monitored parameters indicated a good overall influence for the IW. The injection well design, and K-packer injector design, appear to have functioned well in the implementation, and an 8- to 15-foot radial influence for a possible full-scale design appears reasonable. IW segmentation appears to have facilitated adequate contact of reagents with the VOHs, and the monitoring of numerous target area and surrounding wells provided ample data to verify field study effectiveness.

Overall field study success is attributed to thorough site delineation beforehand, selection of an effective and controllable chemical oxidation process, use of an injection technique that ensures adequate reagent distribution, and a broad-based monitoring program to deliver the quantity and variety of data needed to evaluate process performance.