

Chemical Oxidation of Tetrachloroethene (PCE) Contamination in a Fractured Saproplitic Bedrock Aquifer Using Fenton's Reagent and Sodium Permanganate

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Abstract: This describes the progressive remediation of a PCE contaminant plume using two separate chemical oxidizers in a fractured saprolitic bedrock aquifer in Rockville, Maryland. The geology consists of fine-grained soils overlying weathered-fractured schist and phyllitic bedrock (saprolite). The state of Maryland required that the onsite source be remediated to a risk-based PCE cleanup goal of 253 micrograms per liter (ug/L) and allowed natural attenuation as the offsite remedial action. The source area remediation was initially performed using a Fenton's Reagent-based chemical oxidation process. A successful bench test and a field scale pilot test were conducted prior to implementing a full-scale program that used ten stainless steel treatment wells. The initial post-treatment results looked promising, but the contaminant concentrations increased (rebounded) significantly following the treatment process. The October 2000 (rebound) PCE contaminant concentrations in the aquifer ranged from 7.8 ug/l to 26 milligrams per liter (mg/L), averaging 8.5 mg/L, as determined from 17 sample points. In response to these rebound concentrations, 11,000 pounds (lbs.) of liquid sodium permanganate were injected into the aquifer at 50 locations in late January 2001. This successful treatment application resulted in an 89.3 percent average PCE reduction in the aquifer with an average concentration of 909 ug/L by late February 2001.

Chemical oxidizers (CO) are being used with increasing frequency to remediate chlorinated organic contaminants (Clayton, 2000). These applications have achieved various degrees of success. The successful remediation of PCE contamination in a fractured saprolitic bedrock aquifer was accomplished through the progressive applications of two separate CO. The first CO application used a Fenton's Reagent based process that resulted in limited contaminant reduction due to the complexities of the geologic conditions. The second more successful CO application was performed by injecting liquid sodium permanganate as a 20 percent concentration solution into the aquifer, which resulted in a substantial contaminant reduction.

In situ chemical oxidation was used to remediate dissolved phase (PCE and associated degradation by-products) contamination at a commercial property (site) that was formerly occupied by a dry cleaner, a casket manufacturer, an auto repair shop, and a restaurant. The site is underlain by up to 8.5 feet of fine-grained soils and highly weathered to decomposed saprolitic soils overlying weathered and fractured schist and phyllitic bedrock. The saprolitic metamorphic bedrock contains subvertical fractures and foliation and subhorizontal cross cutting fractures. The strike of the foliation is southwest to northeast and dips 75 to 80 degrees northwest. The resulting vector component of groundwater flow is to the west with an upward flow component. Groundwater flow primarily occurs in the shallow fractured saprolitic aquifer to a depth of 30 plus feet bgs with lesser amounts of flow occurring in the deeper fractured competent bedrock. The decreased groundwater flow with increasing depth is caused by fracture apertures that are healed (closed) or in-filled with clay. As a result both the fractures and the rock matrix have low hydraulic conductivities.

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The groundwater contamination present at the site is primarily dissolved PCE with lesser concentrations of degradation by-products. Groundwater sampling data indicated rapid degradation of the onsite contaminants in a flow system where the contaminant transport was determined to be between 0.25 and 0.75 foot per day. The dissolved phase PCE concentration data in groundwater prior to remediation ranged from the low ug/L range to 3.7 mg/L in December 1998 and March 1999. Based on analysis of the contaminant distribution, the source area was believed to be located in the area surrounding and upgradient of treatment well TW-1 (Figure 1). The PCE release may have resulted from contaminated water leaking from terracotta sewer pipes and/or from a release to surface soil that may have been excavated during site regrading activities. The residual onsite dissolved phase groundwater contamination is thought to be a result of the matrix diffusion, where the contaminants are being slowly and continuously released back into the groundwater flow system from the saprolitic matrix. The original PCE release entered the soil and subsequently the saprolitic rock matrix via the secondary porosity of the foliation and fracture network and then, over time became sorbed (absorbed and adsorbed) into the primary porosity of the rock matrix. Thus, in order for the remediation to be successful both the primary and secondary porosity of the matrix had to be addressed under a remediation program.

In April 1999 a risk-based corrective action plan was developed for the site based on the current and future use scenarios. Natural attenuation was accepted as the recommended remedial option for the offsite contamination due to strong evidence of natural biodegradation. An onsite risk-based clean-up goal was calculated at 253 ug/L of PCE in the groundwater. The risk-based clean-up goal was approved by the regulatory agency, but required that onsite remediation be conducted. Insitu chemical oxidation using Fenton's Reagent (FR) was selected as the preferred remediation because the cleanup period was thought to be very rapid, if successful. The FR option was successfully demonstrated during a bench scale test and then was further evaluated during a 10-day field scale pilot test where the oxidation results; again looked very promising. These apparently successful results lead to the implementation of a full-scale chemical oxidation program involving the use of 10 stainless steel treatment wells. The initial post-treatment results looked promising, but the contaminant concentrations increased (rebounded) significantly following treatment process. This contaminant rebound occurred because the solvents which had been previously bound to the soil and rock matrices were desorbed from the aquifer matrix and released in the groundwater by the heat generated during the Fenton's Reagent process. The resulting rebound concentrations were observed in the October 2000 sampling data results shown in Figure 1.

After further analysis of the data and the flow and contaminant transport processes in the aquifer matrix, a different chemical oxidizer (sodium permanganate) was selected to address the remaining PCE contamination. Sodium permanganate (LIQUOX™) was selected over potassium permanganate because it could be delivered to the aquifer at a higher dosage concentration (Amarante, 2000). The sodium permanganate remediation program involved injecting a 20 percent solution of liquid sodium permanganate (NaMnO₄) with a specific gravity between 1.15 and 1.2. It was anticipated that the injection of this high density NaMnO₄ solution (compared to water) would invade the secondary porosity of the fractured aquifer network and potentially follow similar flow paths as occurred during the original solvent release into the aquifer. The NaMnO₄ solution was injected at 50 grid-derived locations in late January 2001. The injection volume was based on the weight percentage of sodium required for the estimated oxidation of target contamination as per discussions with the chemical manufacturer's representative David Amarante. A total of 11,000 lbs. of NaMnO₄ (4,400 lbs. of

sodium) were injected into the aquifer through the use of direct-push equipment and by manual addition to existing wells. The injection program was developed as an overlapping grid pattern that used the natural groundwater flow system to disperse the CO throughout the aquifer as groundwater migrated across the site. The first set of post-treatment sampling data, shown in Figure 2 was collected in February 2001 (one month following the treatment application). The contaminant concentration rebound observed using the Fenton's reaction process was not observed during the permanganate treatment phase. The data shown in Figure 2 indicates that there have been significant to almost complete reductions averaging 89.3 percent of the PCE concentrations in groundwater at 12 of the 17 wells sampled. The next round of the sampling scheduled for May 2001 should allow sufficient time for the remaining permanganate to spread through the aquifer resulting in further PCE reductions.

References:

Amarante, D., 2000. Applying In Situ Chemical Oxidation. *Pollution Engineering*, February 2000.
 Amarante, David, Personal Communication, November 2000.
 Clayton, W.S. Marvin, B.K., Pac, T., Mott-Smith, E., 2000, A Multisite Field Performance. Evaluation of In-Situ Chemical Oxidation Using Permanganate, *2nd International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Vol C2-6, pp.101-108
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