Fractured Crystalline Bedrock Ground Water Remediation of Dissolved TCE via Sodium Permanganate Solution Injection & Re-circulation.

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Abstract

In situ chemical oxidation (ISCO) is an emergent remedial technology where organic contaminants are degraded in the subsurface via contact with chemical oxidants. Successful implementation of ISCO has been documented in overburden applications where the delivery mechanism provided sufficient oxidant-contaminant contact. The objective of this pilot study was to field test the application of sodium permanganate solution injection and re-circulation (I&R) for remediation of dissolved trichloroethene (TCE) in fractured bedrock ground water. The study entailed the intermittent injection and re-circulation of a sodium permanganate solution through bedrock fractures expressed in open bedrock boreholes and bedrock monitoring wells. Extracted groundwater was dosed with sodium permanganate to create a solution with a 5% concentration that was re-injected back into the fractured bedrock at the contaminant source area. The injected permanganate solution replaced ground water with high concentrations of dissolved TCE (100,000 to 200,000 ug/L), thus allowing continued TCE and permanganate contact via natural advection, dispersion, and diffusion under natural hydraulic gradients. Injected solution was left in the bedrock fracture system until the permanganate was degraded and rebound was observed.

The Site is located in Northeastern, Massachusetts, is approximately 1.75 acres, and is currently vacant. The Site is a former printed electronic component manufacturer where discharges of spent solvents to a former subsurface disposal system had occurred. The Site is characterized by concentrations of TCE in the source area ranging between 1 to 10% of the pure phase solubility. The depth to ground water and bedrock are approximately 15 feet and 45 feet, respectively. The bedrock formation is a gneiss comprised of light gray-white plagioclase feldspar with lenses of quartz and minor biotite mica. Core samples displayed thin to thick veins of calcite, thin veins of pitted pyrite and slickensides with slight offsets. High angle fractures were observed in cores with major fracture spacing between 4 and 6 feet. Based upon the results of site characterization the primary source area at the Site was identified in the vicinity of a former industrial wastewater leachfield at the Site. Intrusive exploration and borehole installation techniques entailed bedrock coring to ascertain fracture frequency and relative dip. Focused hydraulic testing in open boreholes via pneumatic packers demonstrated hydraulic communication in TCE impacted nearby shallow bedrock monitoring wells that indicated fracture interconnectivity in the source area.

Based upon the results of conceptual site model development and remedial alternative identification, chemical oxidation was selected as a remedial alternative for pilot testing to address ground water impacts in the source area at the Site. Sodium permanganate was chosen as an oxidant because it is relatively safer to use than alternatives and does not require addition of catalysts or pH adjustment. Both injection and re-circulation were implemented in order to better control the distribution of the permanganate in the fractured bedrock aquifer. Overburden and bedrock hydraulic gradients were monitored via down-hole pressure transducers to determine any potential changes to TCE migration and/or gradients caused by the I&R of the solution.

Post I&R groundwater sampling data indicated concentrations of TCE were reduced from between 100,000 to 150,000 ug/L to below 1 ug/L in the injection well. Concentrations in monitoring wells were reduced from approximately 150,000 ug/L to less than 1 ug/L initially and to between 30,000 and 50,000 ug/L once rebound occurred. Post I&R monitoring did not indicate uncontrolled migration of the permanganate solution. Full-scale source area implementation is currently in progress and is comprised of two additional open bedrock boreholes, injection and extraction manifolds with flow monitoring devices and pressure gauges, and permanganate dosing and injection equipment. Ongoing full-scale implementation and monitoring is projected to occur over the next two years.

Introduction:

In situ chemical oxidation (ISCO) is an emergent remedial technology for the degradation of organic contaminants in the subsurface via contact with chemical oxidants. Successful implementation of ISCO has been documented in published literature for overburden applications where the delivery mechanism provided sufficient oxidant-contaminant contact. Many published laboratory and field studies have focused on implementation of ISCO in unconsolidated relatively permeable environments. This study focuses on implementation of ISCO in a crystalline fractured rock environment.

The objective of this pilot study was to field test the application of sodium permanganate solution injection and recirculation (I&R) for remediation of dissolved trichloroethene (TCE) in fractured bedrock environment. The study entailed the intermittent injection and recirculation of a sodium permanganate (permanganate) solution through bedrock fractures expressed in open bedrock boreholes and bedrock monitoring wells.

The Site is a former electronic component manufacturing facility located in Northeastern, Massachusetts. Reportedly discharges of spent solvents to a former subsurface disposal system had occurred at the Site. The Site is characterized by concentrations of TCE in the source area ranging between 1 to 10% of the pure phase solubility. The bedrock formation is a gneiss comprised of light gray-white plagioclase feldspar with lenses of quartz and minor biotite mica.

Based upon the results of site characterization the primary source area at the Site was identified in the vicinity of a former industrial wastewater leachfield at the Site. Intrusive exploration and borehole installation techniques entailed bedrock coring to ascertain fracture frequency and relative dip. Focused hydraulic testing in open boreholes via pneumatic packers demonstrated hydraulic communication in TCE impacted nearby bedrock monitoring wells that indicated fracture interconnectivity in the source area.

Based upon the results of conceptual site model development via site characterization and remedial alternative identification, chemical oxidation was selected as a remedial alternative for pilot testing to address ground water impacts in the source area at the Site. Sodium permanganate was chosen as an oxidant because it is relatively safer to use than alternatives and does not require addition of catalysts or pH adjustment. Both injection and re-circulation were implemented in order to better control the distribution of the permanganate in the fractured bedrock aquifer. Overburden and bedrock hydraulic gradients were monitored via down-hole pressure transducers to identify any potential changes to TCE migration and/or gradients caused by the test so that corrective action would be undertaken as needed. Close monitoring was required to comply with Massachusetts Contingency Plan (MCP) requirements regarding the application of groundwater remedial additives.

Extracted groundwater was dosed with sodium permanganate to create a solution with a 5% concentration that was re-injected back into the fractured bedrock at the contaminant source area. The injected permanganate solution replaced ground water with high concentrations of dissolved TCE (100,000 to 200,000 ug/L), thus allowing continued TCE and permanganate contact via natural advection, dispersion, and diffusion under natural hydraulic gradients. Injected solution was left in the bedrock fracture system until the permanganate was degraded and TCE rebound was observed.

Site Description and Characterization:

The Site is located in Northeastern, Massachusetts, is approximately 1.75 acres, and is currently vacant. The Site is a former printed electronic component manufacturer where discharges of spent solvents to a former subsurface disposal system had occurred. The facility ceased operations in 1988 and releases of solvents were assumed to have occurred from the 1960s to 1970s. There are two surface water bodies located approximately 750 ft to the north and northwest of the Site. Both ponds are reportedly used for recreational purposes and are not active or potential potable water sources.

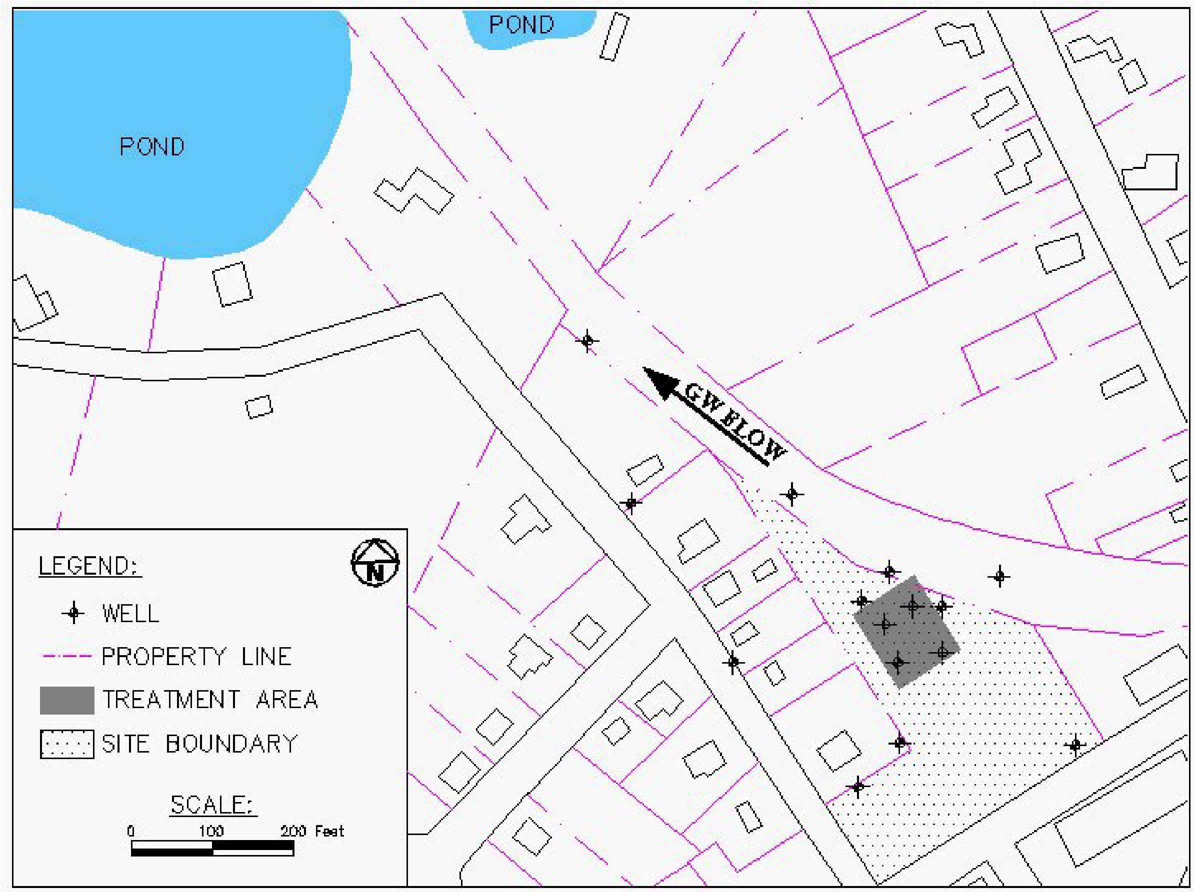


Figure 1. Site Map showing Site boundary, treatment area, and well locations.

Fractured Bedrock Characterization:

Topographic, geologic, and aerial photographic information and data were reviewed to evaluate bedrock structure of the Site area. Collection of lineament data and reproducibility tests were performed by overlaying lineament maps and identifying lineaments which were coincident. Coincident lineaments were then overlain onto the Site and analyzed to evaluate how apparent lineaments/fractures affect Site contaminant hydrogeology. Identified lineaments appeared to be cultural features like roads and power lines and natural features like streams and steep topographic changes. Fracture trace analysis was corroborated through mapping of outcrops near the site, which provided additional information about bedrock fractures and fracture orientation, and whether outcrop observations correlated with fracture trace analysis and bedrock cores. Measured structural features did not coincide with the apparent strike of identified lineaments. Lack of identified lineaments in the Site area was attributed to the relatively thick sequence of glacial outwash deposits overlying bedrock structure in the Site area.

Drilling Methods and Observed Geology

The unconsolidated deposits encountered during drilling of monitoring wells consisted of a loose-to-compact, moderately well sorted, coarse-to-fine sand with varying amounts of rounded gravel and traces of silt. This deposit is representative of glacial outwash deposits in the area and continued to the top of bedrock. The sand and gravel generally ranged in thickness from 45 to 50 ft in the borings that were continued into or onto the top of bedrock. No glacial till unit was found beneath this layer on top of the rock, indicating that the layer was likely deposited as glacial outwash. The layer also exhibited a moderate yield of groundwater during well development due to the coarse, well sorted grain size distribution.

Six bedrock groundwater monitoring wells and three bedrock boreholes have been installed on the Site to assess bedrock groundwater quality and implement remedial activities. Intrusive exploration and borehole installation techniques entailed air-rotary drilling and bedrock coring to ascertain fracture frequency and relative dip.
The bedrock cores were advanced utilizing a hollow-stem auger drilling rig with a 4-inch wire-line core barrel. Overburden boring advancement was accomplished by hollow stem auger to the top of the bedrock surface (45 feet) and a 5-inch casing was advanced to and seated 4 feet into the bedrock. Bedrock coring was accomplished by 4-inch wire-line coring through the bedrock up to 80 feet below grade.

The bedrock formation was observed to be a gneiss comprised of light gray-white plagioclase feldspar with lenses of quartz and minor biotite mica. Bedrock core samples displayed thin to thick veins of calcite, thin veins of pitted pyrite and slickensides with slight offsets. Relatively high angle fractures were observed in cores with major fracture spacing between 4 and 6 feet.

Groundwater Hydraulics and Packer Testing

The depth to ground water and bedrock are approximately 15 feet and 45 feet, respectively. Pneumatic straddle packer testing was performed on fractured zones encountered during rock coring. The testing consisted of installing a 12- foot long packer assembly comprised of a 4-foot long lower packer, 6-foot long upper packer, and 2-foot screened interval. Once the packer assembly was installed at each fractured interval, the packers were inflated with nitrogen gas, 50 to 60 feet of 2-inch PVC riser pipe was threaded into the top of the packer, and a submersible pump was engaged and lowered slowly through the water column to evacuate standing water and to purge three well volumes. Prior to pumping pressure transducers were installed in nearby shallow bedrock monitoring wells to monitor changes in hydraulic head. After purging, groundwater samples were collected for field screening via gas chromatography and subsequent confirmatory laboratory analysis.

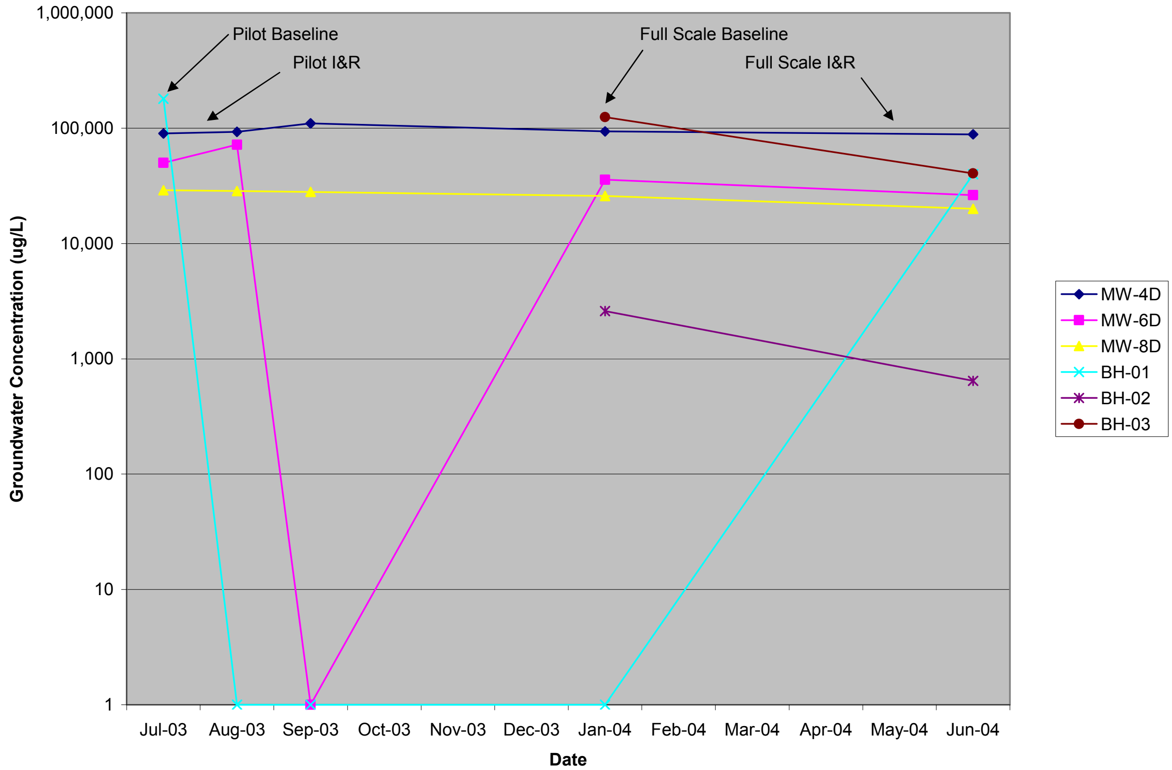
During packer testing each fractured interval was pumped at a rate of approximately 1 gallon per minute (gpm). Drawdown measurements during pumping were recorded for each fractured interval. Pressure transducer data indicated hydraulic connection between the open boreholes and shallow bedrock monitoring wells. The largest changes in hydraulic head were measured at the 60-70 ft fractured interval depth, possibly indicating a more direct hydraulic communication between wells set at that depth interval.

Groundwater Analytical Results and Contaminant Distribution

At borehole BH-01 TCE was detected in all three fractured intervals sampled. TCE concentrations of 9,200, 23,000, and 180,000 ug/L were reported at the 57 ft, 62 ft, and 67 ft depths, respectively. At BH-02 TCE concentrations of 60, 1,600, and 900 ug/L were reported in the 55 ft, 65 ft, and 75 ft depths, respectively. At BH-03 TCE concentrations of 104,000 and 18,000 ug/L were reported at the 65 ft and 75 ft depths, respectively.

The Site is characterized by concentrations of TCE in the source area ranging between 1 to 10% of the pure phase solubility. TCE was the constituent detected at both the highest concentration and frequency of detection. TCE was detected at the highest concentrations in wells situated down-gradient (55,000 ug/l) and proximate (180,000 ug/l) to the former subsurface wastewater disposal system. Decreasing TCE concentrations were observed at wells located approximately 250 feet (29,000 ug/l) and 600 feet (12,000 ug/l) downgradient of the treatment area. Based upon the results of site characterization, the primary source area at the Site was considered to be the area of the former industrial wastewater leachfield at the Site located in the vicinity of BH-02.

Figure 2
TCE Groundwater Concentrations



Remedial Methodology:

The objective of this test was to evaluate the application of sodium permanganate solution injection for remediation of dissolved chlorinated ethenes in groundwater via in-situ chemical oxidation, specifically TCE, present in the shallow bedrock aquifer. Based upon the results of the remedial alternative evaluation the type and concentrations of OHM present in shallow bedrock ground water at the Site, and the nature of the shallow fractured bedrock aquifer at the Site, chemical oxidation using sodium permanganate was selected as a remedial alternative for further evaluation to address ground water impacts in the source area at the Site. Since exposure scenario concentrations for soil and overburden groundwater at the site were below applicable regulatory standards, active remediation of the unsaturated zone and overburden groundwater was not warranted. It is anticipated that monitored natural attenuation (MNA) will further confirm that dissolved VOC concentrations in the overburden groundwater and shallow bedrock aquifer downgradient from the source area will comply with applicable standards on a long-term basis.

Monitoring:

Baseline chemical monitoring to characterize pre-pilot Site conditions included analyses for VOCs and dissolved iron and manganese. Baseline monitoring events were conducted in July 2003 for the pilot test and January 2004 for additional boreholes and full scale implementation. Hydraulic monitoring was performed via down-hole pressure transducers to monitor gradients in the shallow bedrock and saturated overburden at locations both up-gradient and down-gradient of the injection and recirculation area. Results of continuous hydraulic monitoring via electronic pressure transducers in monitoring wells screened in the shallow and deep overburden and 250 feet downgradient did not indicate noticeable change in hydraulic gradients observed as a result of the injection process. Observed head measurements indicated a general decreasing trend during injection and recirculation activities. Extraction rates were set levels exceeding injection rates which likely contributed to decreasing hydraulic head observed in nearby monitoring wells. The injection and recirculation process, established to assert hydraulic control and prevent groundwater mounding, appeared to be effective based on the observed field data.

Post-injection monitoring was undertaken to evaluate contaminant distribution, to monitor rebound in VOC concentrations, to confirm no adverse impacts to off-Site groundwater quality, and to monitor secondary drinking water standards of iron and manganese. Post-injection monitoring included VOCs by EPA Method 8260B and dissolved iron and manganese.

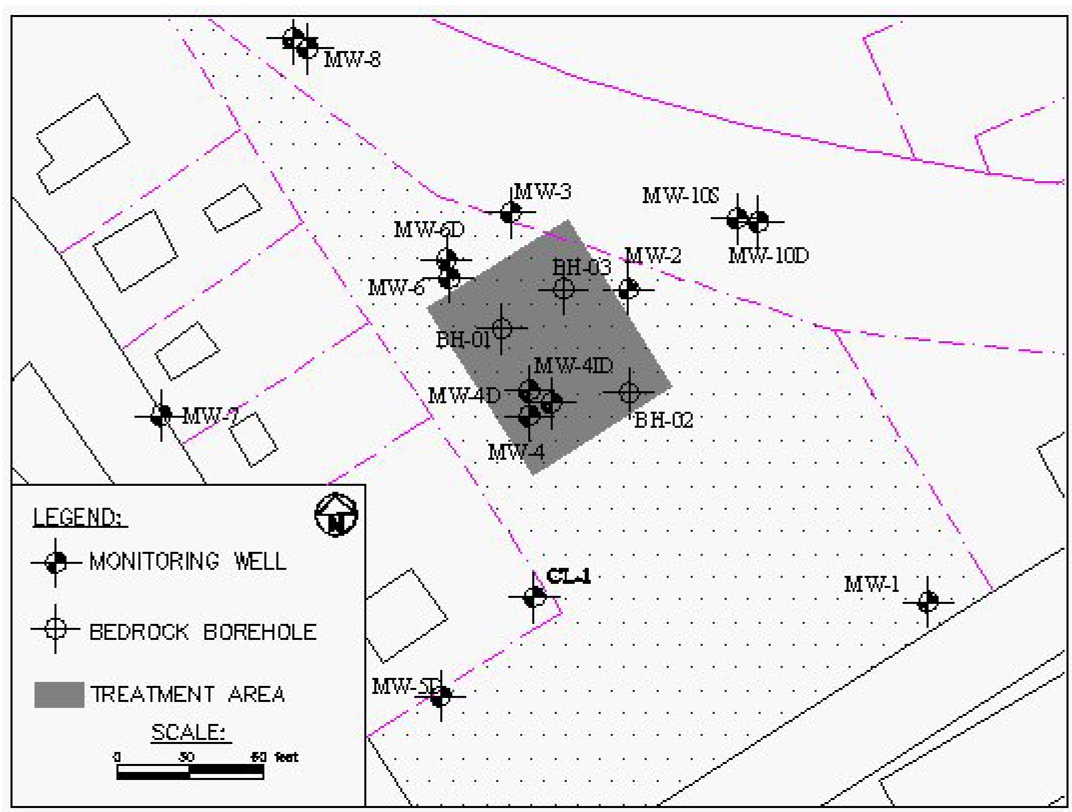


Figure 3. Site Map showing monitoring wells and bedrock boreholes.

Injection and Re-circulation:

This remedial alternative entailed the injection of a 5% sodium permanganate solution into an approximately 100-foot by 40-foot source area. The treatment goal was to reduce shallow bedrock ground water impacts through the injection of liquid sodium permanganate solution into the shallow bedrock fracture system via hydraulically isolated fracture expressions in open bedrock boreholes. Focused hydraulic packer tests demonstrated hydraulic communication between bedrock boreholes and existing monitoring wells indicative of fracture interconnectivity in the source area. The injection and recirculation process produced extracted groundwater from shallow bedrock monitoring wells that provided dilution water for the makeup of permanganate solution. The pilot solution mixing process entailed metering 40% Permanganate solution into extracted groundwater in order to dilute the solution down to an approximate concentration of 5%.

Estimating the required solution strength of permanganate entailed estimating the mass of TCE in the shallow fractured bedrock. The mass of TCE calculation entailed averaging Site concentration data, defining a source area and thickness, and selecting an appropriate shallow bedrock porosity. An approximate average groundwater concentration of TCE in the shallow bedrock source area was derived from the average of reported concentrations from monitoring wells MW-4D and MW-6D, and the highest concentration obtained during hydraulic packer testing of BH-01. An approximate area of the shallow bedrock source area was defined by approximating an oblong shaped area that encompasses shallow bedrock monitoring wells with TCE concentrations that have historically exceeded 100,000 ug/L. The shallow fractured bedrock source area thickness was derived from the average depth into bedrock of wells MW-4D, MW-6D, and BH-01. A porosity of the shallow fractured bedrock source area was based on the relative fracture frequency.

Based on published literature review a ratio for permanganate to TCE of 5 to 1 and solution injection concentration percentage of 5% were chosen initially. A solution concentration of 5% was chosen to minimize the precipitation of MnO_2 and estimated extraction rates indicated application could be achieved in one day. The mass of permanganate required was calculated by multiplying the calculated mols of TCE by the aforementioned stoichiometric ratio which represents a 40% oxidation efficiency based on hypothetical stoichiometric calculations. 100 gallons of 40% permanganate solution were used and injected as approximately 800 gallons of 5% solution. The actual volume of injected dilute permanganate solution was greater because of rinsing of injection and recirculation equipment.

Based on results of groundwater monitoring data collected from one day to two weeks after initial injection, concentrations of TCE in MW-6D had begun to increase from slightly below baseline levels to levels significantly above baseline levels. Monitoring data and observations from BH-01 indicated reduction of VOCs to below laboratory method detection limits initially and a relatively concentrated permanganate present after one month. One month later re-circulation only was employed in order to re-distribute Permanganate located in the vicinity of BH-01 toward MW-4D and MW-6D by pumping groundwater directly from MW-4D and MW-6D into the injection well BH-01. Wells MW-4D and MW-6D were pumped at approximately 1 to 1.5 gallons per minute resulting in an injection rate of 2 to 3 gpm into BH-01. After approximately 30 minutes of recirculation light brown groundwater was observed pumping from MW-6D indicating the presence of the manganese dioxide ($Mn0_2$), an oxidation reaction byproduct, suspended in the groundwater. After approximately 45 minutes light purple groundwater (indicating the presence of dilute permanganate) was observed pumping from MW-6D. Groundwater re-circulation was continued for approximately 4 hours. Neither, light brown colored groundwater or purple colored groundwater was pumped from MW-4D.

Full scale implementation of the remedial process began in April 2004 which included the injection of a more dilute (~1%) solution and adding open boreholes BH-02 and BH-03 into the re-circulation process. The injection and recirculation process produced extracted groundwater from shallow bedrock monitoring wells MW-4D, MW-6D, and MW-8D which provided dilution water for the makeup of permanganate solution. The full scale solution mixing process entailed metering 40% Permanganate solution into extracted groundwater in order to dilute the solution down to an approximate concentration of 1%. Extraction rates from monitoring wells and selected injection boreholes were approximately 1 to 2 gpm from each well, injection rates ranged from 1 to 2 gpm for each injection borehole. Various I&R scenarios are being implemented and evaluated to optimize permanganate distribution in the fractured bedrock based on the June 2004 chemical monitoring.

Wastewater and remediation wastes were not generated because the groundwater extracted in the re-circulation process was used for dilution of the 40% solution which provided treatment via contact with permanganate. The permanganate solution comprised of extracted groundwater was then injected back into the subsurface during the process.

Field/Pilot Test Monitoring Results:

Observations made during field/pilot testing of the injection and recirculation process indicated hydraulic connection between injection well BH-01 and monitoring well MW-6D. Observations included the presence of light brown suspended sediment (MnO_2) in groundwater extracted from MW-6D and subsequently darker purple colored groundwater indicating permanganate that was injected into the BH-01 had been distributed to MW-6D under recirculation conditions. As a result a more dilute concentration of permanganate was delivered to fractured system in the vicinity of MW-6D initially. Observed reduction in concentrations of TCE were approximately one order of magnitude lower (from 55,000 ug/L to 6,800 ug/L).

Post-injection monitoring data from the injection well (BH-01) indicated that TCE concentration had been reduced from between baseline conditions (ranging from 9,200 to 180,000 ug/L in the three fracture zones tested) to below laboratory method detection limits (0.5 to 1.0 ug/L). Data from the monitoring well MW-6D indicated concentrations of TCE had been reduced from between baseline and pre-recirculation concentrations (55,000 ug/L) to below laboratory method detection limits (0.5 ug/L) and rebounding to 6,800 ug/L. Initial water samples extracted from the injection well water column were dark brown indicating significant precipitation of MnO_2 likely as a result of high solution strength. Subsequent water samples contained more concentrated permanganate resulting in a dark purple color and without suspended sediment.

Post-injection monitoring data from the monitoring well MW-4D indicated no measurable reduction in the concentration had been observed. Initial water samples extracted from the injection well water column did not contain any suspended MnO_2 sediment or display any purple coloration. These results are attributed to MW-4D being located upgradient of the injection hole, being screened at an elevation approximately 10-feet higher than the injection well and MW-6D. Therefore it appeared that there is no relatively direct connection between the fractures expressed in injection well BH-01 and those expressed in MW-4D. Levels of dissolved iron and manganese in groundwater were above baseline levels in the injection boreholes and consistent with baseline levels in monitoring wells.

Overall, results to date indicate that in-situ oxidation via permanganate delivery is a viable remedial alternative for the reduction of TCE, DCE, and PCE concentrations in fractured bedrock groundwater. The pilot study and initial full scale implementation has demonstrated that sodium permanganate at between 1 and 5% solution will oxidize these VOCs at the concentrations observed in the shallow bedrock groundwater of the suspected release source area. The I&R process appears to enhance oxidant-contaminant contact by demonstrating delivery to at least some fractures expressed in common boreholes and monitoring wells.

Conclusions:

Post I&R groundwater sampling data indicated concentrations of TCE were reduced from between 100,000 to 150,000 ug/L to below 1 ug/L in the injection well initially and to between 30,000 and 50,000 ug/L once rebound occurred. Ongoing chemical and hydraulic monitoring of I&R implementation did not indicate uncontrolled distribution of the permanganate solution or significant alteration of the fractured bedrock flow system. Full-scale source area implementation is currently in progress and is comprised of two additional open bedrock boreholes, injection and extraction manifolds with flow monitoring devices and pressure gauges, and permanganate dosing and injection equipment. Some reduction in permeability was observed initially in BH-01 and was attributed to injection of the 5% solution. Consequently the permanganate solution concentration has been reduced to 1%. Positive results of the initial pilot test spawned a full scale remedy implementation at the Site. Lessons learned in the pilot test were incorporated into the full scale remedial design and will be incorporated into full scale implementation. Ongoing full-scale implementation and monitoring is projected to occur over the next two years.