Field Pilot Test of In Situ Chemical Oxidation through Recirculation using Vertical Wells at the Portsmouth Gaseous Diffusion Plant

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Introduction

In situ chemical oxidation is an emerging remediation technique in which chemical oxidants are delivered to the subsurface to rapidly degrade organic contaminants (Siegrist 1998, US EPA 1998). For the past 6 years, engineers and scientists at Oak Ridge National Laboratory (ORNL) have been developing this technology for in situ degradation of organic chemicals such as trichloroethene (TCE), perchloroethene (PCE), naphthalene, and pyrene (Gates and Siegrist 1995; West et al. 1997); Siegrist et al. 1998a and 1998b). Laboratory-scale experiments performed to date have demonstrated that permanganate (MnO_4^-), if applied at sufficient loadings, can effectively oxidize TCE and PCE. The following describes the overall chemical reaction for the oxidation of TCE using potassium permanganate (eqn.1):

$$2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 + 2MnO_2 + 2KCl + HCl \qquad (1)$$

Permanganate is commonly used in waste water treatment to oxidize organic compounds and is commercially available in two forms, $KMnO_4$ and $NaMnO_4$. While the behavior and oxidation potential of the two compounds is similar, the aqueous solubility of $NaMnO_4$ is much higher (~50% vs. ~6%). The relative stability of MnO_4^- makes it attractive as an in situ chemical oxidant since it can be delivered and dispersed in soil and groundwater and has the ability to migrate by diffusion into fine-grained zones where residual contaminants may exist.

To continue development of in situ chemical oxidation for widespread use and commercial viability, techniques for delivering chemical oxidants in adequate amounts to the subsurface are being developed (Case, 1998; DOE 1996a; Gates and Siegrist 1995; Lowe et al. 1998; Siegrist et al. 1994, 1995, 1998a, 1998b, 1999; Struse 1999; West et al. 1995). Initially, an in situ chemical oxidation through recirculation (ISCOR) treatability study was conducted at the U.S. Department of Energy Portsmouth Gaseous Diffusion Plant (PORTS), Piketon, Ohio, involving injection and recirculation of an oxidant solution (~2wt.% $KMnO_4$) through paired horizontal wells and selected vertical wells (West et al. 1997). Although oxidant delivery/recirculation was impacted by heterogeneity within the demonstration area, where the oxidant was able to permeate the aquifer, significant and sustained reductions in TCE were measured in soil and ground water. The goal of this field pilot test was to test an alternative oxidant delivery approach using recirculation via vertical wells in a 5-spot pattern to develop a sufficient understanding of ISCOR to facilitate completion of the Corrective Measures Study process. The test design was comprised of a 5-spot vertical well pattern with the central well serving as the injection point (Figure 1).

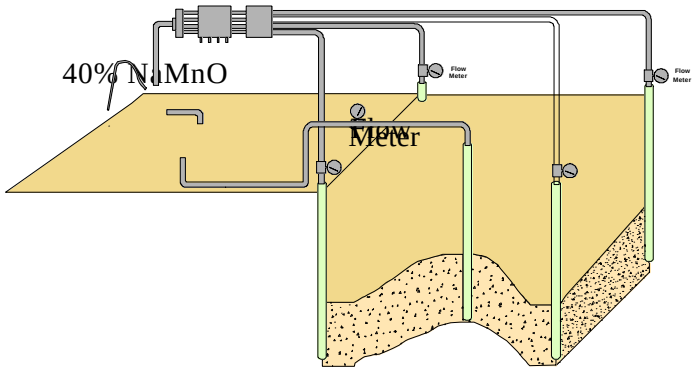

Figure 1. Conceptual diagram of vertical well injection/recirculation system.

The four corner extraction wells were placed in a square grid surrounding the injection point on a fixed radius of 45 ft. Several monitoring wells were also installed throughout the region to monitor changes in contaminant concentrations, oxidant concentrations, water quality parameters, and water levels during operation. The system was designed to accommodate recirculation flow rates of 2 to 20 gpm supplemented with $NaMnO_4$ to maintain delivery of the oxidant concentration at ~250 mg $NaMnO_4$ per L of re-injected groundwater.

The advantages of the use of liquid $NaMnO_4$ and a vertical well recirculation approach include: (1) better control of oxidant and contaminant migration within the treatment zone when compared to single well injections, (2) the introduction of higher volumes of oxidant solutions in a given time because existing soil pore water is extracted concurrent to oxidant injection, (3) easier oxidant handling, and (4) potentially lower overall cost for treating larger volumes.

Methods

The field pilot test was conducted within the source area of the 5-Unit Investigative Area, immediately south of the X-770 Building, at PORTS. The geology under the pilot test cell area is comprised of 23-26 ft of Minford sediments underlain by 3 to 8 ft of Gallia. Both units are unconsolidated, Quaternary age members of the Teays formation. The Gallia lithology is typically comprised of a saturated silty-sandy gravel unit of higher permeability overlying a drier lithified unit of coarse angular gravel in a silty clay matrix. The upper more permeable member of the Gallia varies in thickness from 0.5 to 2.5 ft. The Gallia is thicker and more permeable across the southern two thirds of the test cell area. In general, 5-Unit Area groundwater flows horizontally from north to south and the hydraulic gradient is very low (0.001) because of the flat valley floor, the presence of thicker and more permeable Gallia deposits, and the proximity of the east-west-trending groundwater divide present along the central part of the facility.

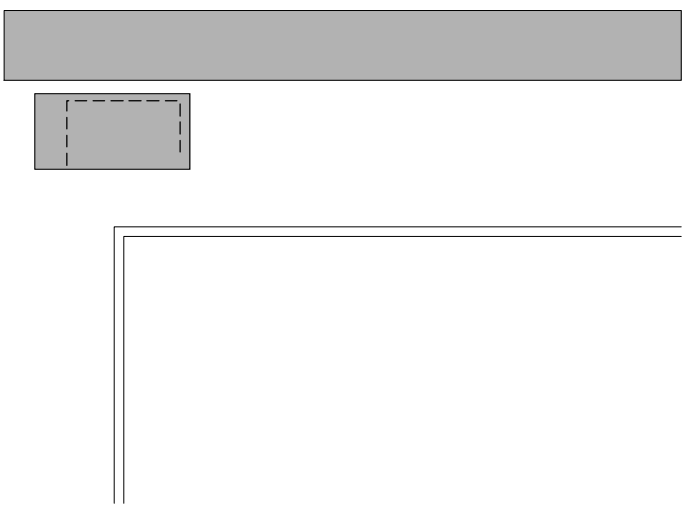

Figure 2. Field pilot test site.

The field pilot test required the installation, development, and hydraulic testing of wells, baseline soil and groundwater characterization, and assembly of the oxidant delivery system. One 6-in diameter injection well, four 4-in diameter extraction wells and nine 2-in diameter monitoring wells to monitor the pilot test operations were installed (Figure 2). Soil and ground water characteristics, physical and chemical, were obtained throughout the area prior to recirculation. Hydraulic tests (pressure injection test and single well tests) were performed to select the recirculation pumping and injection rate and to determine the distribution of permeability within the test area.

A conservative tracer (bromide) was added at the initiation of injection/recirculation to enable detection of the injected water within the treatment area. Approximately 500 gals of 1800 mg/L bromide solution were injected at 18 gpm into the central injection well with equal extraction (4.5 gal/min) at the four corner extraction wells. Concurrently, groundwater samples were collected from each monitoring location and extraction well and analyzed for bromide using an ion selective electrode at 15 to 30 minute intervals until movement of the bromide past the monitoring location was detected. This information was used to determine preferential flow paths, to measure the extent of hydraulic control in the treatment area, and to define the rate and extent of anticipated $NaMnO_4$ transport.

The oxidant delivery system was assembled along the northern side of the test cell. The major components of the system comprise flow and pressure control, oxidant dosing and delivery, and sample ports. System flow rates, pressures, water levels, oxidant feed concentrations, movement/reaction of the oxidant through the Gallia aquifer during recirculation, and contaminant concentrations were monitored daily. Additional analyses for cations, anions, and water quality parameters were collected during recirculation of the first pore volume, but terminated after delivery of the oxidant throughout the test area due to interferences in the analysis method.

During injection and recirculation, oxidant solution was injected into the Gallia through the central well and extracted at equal rates from the 4 perimeter wells located at 45 ft from the central injection well. Groundwater was extracted from the four perimeter wells at a maximum combined rate of 18 gpm (4.5 gpm from each extraction well). Groundwater from the four extraction wells was pumped through a manifold system into a single line where the $NaMnO_4$ solution was added with an oxidant-resistant chemical metering pump. The metering pump was adjusted to feed the concentrated stock solution at a rate sufficient to maintain 250 mg/L of $NaMnO_4$ in the injection water. The oxidant-laden water was then pumped into a 120 gal holding tank providing approximately 7 minutes of residence time for the oxidant with the contaminated groundwater. This ensured that only treated water was re-injected into the aquifer. Injection of the extracted water was permissible as long as the extracted water had been "treated".

A 250 mg/L $NaMnO_4$ solution was recirculated at 18 gpm for the 1st pore volume (approximately 82,000 gals or 3 days). Then the recirculated water with residual $NaMnO_4$ was supplemented with approximately 100 mg/L of $NaMnO_4$ solution to maintain a delivery of ~200 to 250 mg/L of oxidant into the region at 18 gpm for the 2nd and 3rd pore volumes. Approximately 78 gals of 40wt% $NaMnO_4$ (162.4 kg $NaMnO_4$) were delivered throughout the test region within 10 days. Approximately 240,660 gals of treated groundwater were recirculated. The recirculation flow rates remained steady throughout the test duration with ~1 gpm reduction in total recirculation flow rate over the course of the 10-day test (Table 1). This gradual but minor decline in the total recirculated flow rate is attributed to injection or extraction well fouling, matrix plugging, pump performance, or clogging/plugging within the system lines (at in-line valves, gauges, etc). Pressures within the system and at the injection well gradually increased over time. The injection pressure at the well head nearly doubled, from 10 psi to 18.5 psi, but remained within safe operating ranges based on optimum flow out of the selected well screen, potential fracturing of the formation, and potential damage to the well construction. It is likely that the gradual increase in system pressures and decline in extraction well flow rates is in part, a result of injection well performance or potential redistribution of fine particles in the formation near the well.

Table 1. Summary of Process Operation Parameters.

Location	Ave. Flow Rate (gpm)	Ave. Pressure (psi)
X770-IW01	17.37	14.5
X770-EW01	4.17	65.4
X770-EW02	4.39	146
X770-EW03	4.36	146
X770-EW04	4.59	150

Performance assessment was based on TCE reduction as determined by characterizing contaminants in the aqueous phase before and after treatment. If VOC mass was substantially reduced by oxidation, then the TCE aqueous levels in the extraction and monitoring wells should also be substantially lower. Groundwater was recirculated through the pilot test area until sufficient oxidant had been delivered or breakthrough of the residual oxidant at the injected concentration (indicating that the $NaMnO_4$ was not being consumed in the aquifer) was observed. The TCE concentrations in the test area were monitored during recirculation and for 24 hrs after recirculation was terminated. Finally, post-treatment groundwater concentrations were monitored weekly for approximately 1 month and once at 2 months after recirculation to determine the potential aquifer rebound effects.

Results

A pressure injection test conducted at the injection well (Bouwer and Rice 1976 and Horner, 1951) indicated that the injection well could sustain recirculation rates up to 26 gpm without exceeding optimum pressures at the well head. Observation of water level fluctuations during the pressure injection test also indicated significant variability in hydraulic conductivity across the 64-ft by 64-ft test area. In relative terms, greater water level increases indicate regions of higher permeability while smaller water level increases indicate regions of lower permeability. Single well tests confirmed the variability and provided a relative measure of permeability with values ranging from approximately 26 to >300 ft /d (Table 2).

Table 2. Single Well Aquifer Testing Results.

Well Number	Ave Pre-Inj ft/day	Ave Post-Inj ft/day
X770-EW02	26.5	26.7
X770-EW03	86.5	87.3
X770-EW04	44	54.3
X770-MW01	148	94
X770-MW03	297.5	271.7
X770-MW05	691.5*	532.3
X770-MW07	202.5	187.7
X770-MW08	121	143
X770-MW10	145	113.7
X770-MW12	--	366.3
X770-MW14	601.5*	337

Bromide tracer test results confirmed the hydraulic tests and indicated that the Gallia is very heterogeneous throughout the test region. The bromide curves from the northern wells tend to flatten out indicating a more heterogeneous flow system and greater dispersion while the curves to the west and south indicate a more pronounced (i.e., sharp) bromide front suggesting a more homogeneous flow system with less dispersion (Figure 3). Additionally, bromide rapidly moved (within two hours) in a southeastern direction as delineated by well X770-MW03, but was not initially detected in X770-EW02,

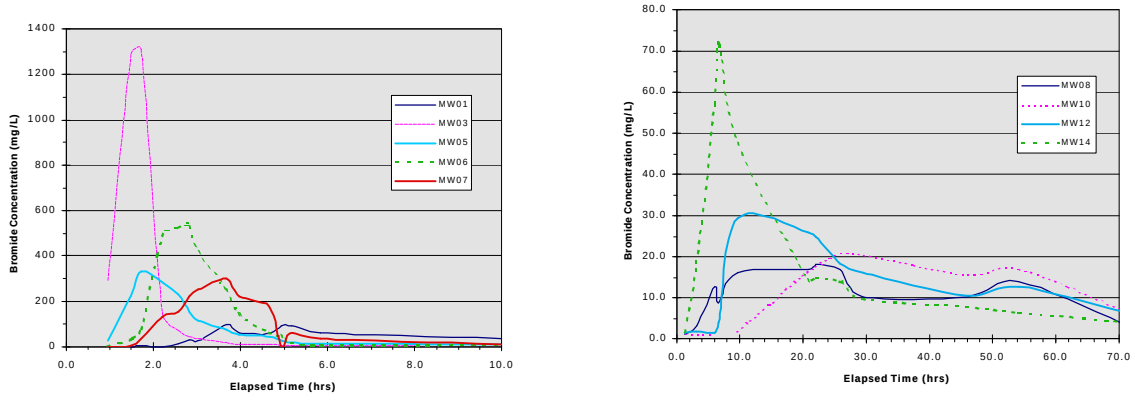

Figure 3. Bromide curves.

the southeastern most well, until 10 hours after injection with the curve peak at ~22 hours after injection. Water levels, measured continuously by a data acquisition system, indicate that the system reached hydraulic equilibrium within a few hours after recirculation was initiated and remained constant throughout the test.

The bromide tracer test also provided insight on the preferential flow paths within the region. Based on preliminary calculations (assuming laminar plug flow and homogenous subsurface conditions) and model predictions (WinTrans) it was estimated that it would take approximately 3 days for the tracer to reach each of the extraction wells located 45 ft away. However, initial detection of the bromide in the extraction wells was within 5 to 10 hours. The tracer was detected at the northeastern well (X770-EW01), but bromide concentrations did not exceed 5 mg/L (near the minimum detection limit of the field probe). Thus, the majority of the water produced from X770-EW01 is presumed to be from outside the test region as indicated by the slow delivery of bromide and oxidant to the well. In relative terms, the region north and east of X770-EW01 appears to be more permeable than the region between the injection well and X770-EW01, including X770-MW10. Finally, the rapid arrival of the bromide tracer at the western extraction wells and the slow arrival at northeastern well illustrates how preferential flow zones control movement of fluids through the Gallia.

Ground water samples collected prior to system operation indicated TCE concentrations ranged from 133 ug/L to 2148 ug/L with higher concentrations detected in the northern and western monitoring wells. Soil samples ranged from 3 to 4527 ug/kg, typically with increasing concentrations with depth. Oxidant injection using vertical wells in a 5-spot pattern was capable of providing sufficient hydraulic control to deliver oxidant throughout the permeable zones of the Gallia within the pilot test area within 3 days or less. The pre-test TCE concentrations throughout the region were reduced to <10 ug/L throughout all but the lower permeable eastern edge of the test region within 3 days indicating an apparent reduction in contaminant levels of ~92% (Figure 4). Continued recirculation for 10 days, provided uniform oxidant delivery throughout the entire area excluding the northeast extraction well (X770-EW01). As of two hours after recirculation was terminated, TCE concentrations were reduced to below detection limits (5 ug/L) at all but one location, (from ~1500 ug/L to 650 ug/L at X770-EW01), indicating an apparent ~97%

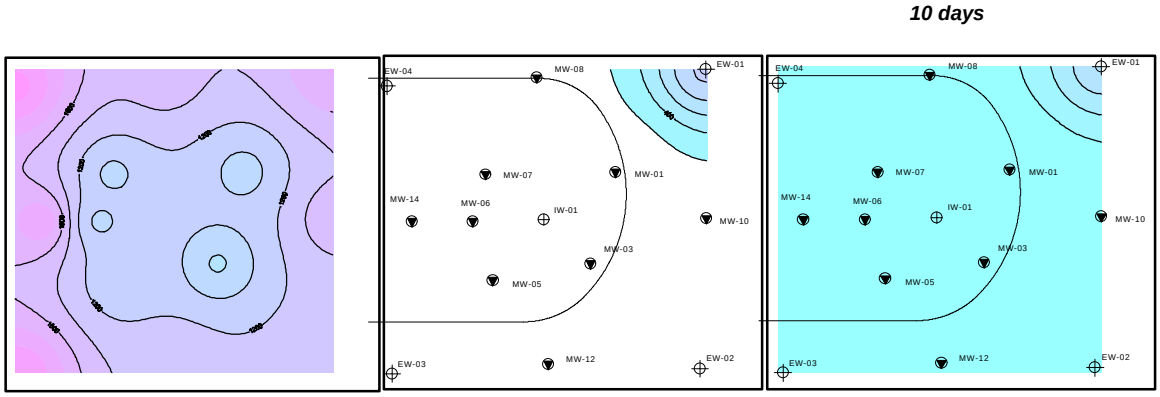

Figure 4. TCE distribution within the pilot test area.

reduction in TCE. When the TCE concentrations are compared to delivered oxidant concentrations (Figure 5) at the same time intervals, the correlation of oxidant delivery with TCE reduction is apparent. The slower arrival of oxidant to the northeast portion of the region (specifically X770-EW01 and X770-MW10) is also noticeable and attributed to the lower permeability of this region. It is important to note that while the permeability of the Gallia varied by over an order of magnitude in the region (Table 2), that oxidant was effectively delivered throughout the area in a relatively short time frame (i.e., 3 days).

To evaluate the short term effects of the residual oxidant and TCE within the region, groundwater samples were collected at 1, 2, 4, 6, 9, 21, and 27 hrs after system shut down. Additionally, groundwater samples were collected weekly for one month after recirculation. Although low levels of TCE were present along the upgradient edge of the test area (14 ug/L at X770-MW08, 39 ug/L at X770-EW04 and up to 738 ug/L at X770-EW01) when the system was shut down, the TCE concentrations continued to decline after recirculation was terminated. This decline in TCE concentrations is due to the oxidation of organic compounds by the oxidant remaining in the pore spaces. TCE remained near or below detection limits (<20 ug/L) for approximately two weeks after recirculation at which point the TCE concentrations along the upgradient northern edge (X770-EW01, X770-MW08, and X770-EW04) and lower permeable eastern edge (X770-MW10) of the test area began to increase (Table 3). The higher concentrations detected at these locations can be attributed to the migration of untreated upgradient plume groundwater into the test region (northern edge) as well as TCE diffusion from the less permeable zones of the test area (eastern edge). It is important to note that near the injection well (15 ft radius monitoring wells) where the delivered oxidant mass was the highest, TCE concentrations remained below detection limits one month after recirculation except at the most upgradient location (35 ug/L at X770-MW01).

Table 3. TCE Concentrations (in ug/L) throughout the Pilot Test Area at Selected Intervals (see Figure 2 for well locations).

Location	**Pre-test baseline (average)**	**3 days after injection (one pore volume)**	**End of inj/rec. (10 d or 3 pore volumes)**	**2 hours after shut down**	**2 weeks after shut down**	**4 weeks after shut down**

One month after system shut down, the oxidant concentrations within the region had declined to less than 1 mg/L while a gradual increase in TCE concentrations was observed. However, the apparent TCE mass reduction within the mobile groundwater fraction of the test cell remained at ~83%. The oxidant consumption over time is as expected and presumed to be due to a combination of factors including oxidation of the natural organic material present and any TCE that was diffusing from the finer grained less permeable zones in the Gallia or the overlying Minford and advecting from the upgradient contamination into the test area.

Efforts to examine reaction intermediates and products (e.g., chlorinated organic acids or partially degraded chlorocarbons) as well as system toxicity have been initiated and revealed no adverse effects. For example, using a Microtox Model 500 analyzer (AZUR Environmental, Carlsbad, CA), groundwater samples were analyzed for acute toxicity to a luminescent bacteria (*Vibrio fischeri*) when exposed to 91% of the total sample concentration. No toxicity was measured for background or post-recirculation samples.

Single well tests were repeated at each monitoring location at the end of the pilot test to quantify any potential formation plugging, possibly due to MnO_2 generation and the potential redistribution of fines within the matrix. Post injection/recirculation hydraulic conductivity values ranged from 26 to 530 ft/d and were not significantly different from the pre-test values (Table 2).

Conclusions

Oxidant injection using vertical wells in a 5-spot pattern was capable of providing sufficient hydraulic control to deliver oxidant throughout the permeable zones of the Gallia within the pilot test area within 3 days. Pre-test baseline TCE concentrations were reduced to <10 ug/L throughout all but the lower permeable eastern edge of the test region within 3 days indicating an apparent reduction in contaminant levels of ~92% within 3 days and ~97% reduction at 10 days (2 hours after the end of the test). This oxidant delivery technique is applicable to relatively permeable, saturated subsurface media contaminated with dissolved and sorbed phase contaminants and potentially ganglia of non-aqueous phase liquids (NAPLs). An underlying aquitard is required in order to prevent spread of contamination during the injection phase. It is noted that application to situations with large masses of NAPLs (e.g., pools) may require substantially higher oxidant loadings and potentially modified hydraulic control approaches.

The costs of the 5-spot ISCOR will vary depending on the scale of the application and the performance goals required. A major cost savings with the recirculation delivery method is avoidance of costs associated with treatment and discharge of extracted ground water, which in this pilot test was ~240,000 gal. The estimated cost per gallon of treated groundwater during the pilot test at a DOE facility was ~$1.70/gal, including well installation costs but excluding PORTS site support (e.g., health and safety, health physics, construction engineering, waste management, and project management oversight). While it is important to recognize that specific site conditions will greatly influence the cost, the most significant costs associated with the 5-spot ISCOR approach are well installation and the oxidant. The cost of the injection wells and extraction wells will be dependent on the size, depth, location, and materials as well as the drilling subcontractor. The cost of the oxidant will be dependent on the oxidant concentration delivered to the subsurface over some period of time based on performance goals and initial contaminant concentrations.

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