In Situ Chemical Oxidation of Volatile Organic Compounds in a Fractured Bedrock Aquifer

Paul D. Rohde, CH2M HILL and Cynthia R. Butler, P.E., CH2M HILL

Abstract

Site Background

A pilot-scale study of in situ chemical oxidation (ISCO) using sodium permanganate is being performed to evaluate the effectiveness of ISCO to remediate volatile organic compounds (VOCs) in a carbonate bedrock aquifer at a site in Davenport, Iowa. The site is an active storage and distribution center for various types of industrial chemicals. The highest concentration of total chlorinated VOCs detected in shallow-bedrock groundwater is 270,500 µg/L, and the highest concentration of total benzene, toluene, ethylbenzene, and xylene (BTEX) compounds detected in onsite shallow-bedrock groundwater is 95,100 µg/L. The concentrations of constituents in several wells suggest the potential presence of light nonaqueous-phase liquid (LNAPL) and dense nonaqueous-phase liquid (DNAPL). Neither of these phases, however, has been observed in groundwater samples collected to date.

The pilot study focused on delivery of sodium permanganate to a depth of 35 feet in the limestone bedrock. This paper presents the design for the ISCO pilot-scale study and summarizes the effectiveness of oxidant delivery and distribution within the shallow limestone bedrock.

ISCO Pilot Study

Results of a pump and treat pilot study conducted previously at the site indicate groundwater extraction is not the preferred remedial alternative due to low sustainable groundwater yields and difficulty verifying complete groundwater capture and gradient control. ISCO is being pilot tested at the site to determine its potential to reduce the high concentrations of VOCs in groundwater. In addition, the pilot study provided data on the ability of low-pressure injection methods to effectively deliver an ISCO solution using permanganate to a fractured bedrock aquifer where there is the potential presence of LNAPL and DNAPL. Sodium permanganate was delivered as a 2 percent and 10 percent permanganate solution. Target permanganate injection concentrations were calculated using measured VOC concentrations in a treatment area of 2,500 square feet to a depth of 35 feet below ground surface (bgs) (i.e., the shallow-bedrock aquifer). Two injection wells were installed with screened intervals in the shallow bedrock aquifer. The monitoring network was supplemented with four 1-inch-diameter piezometers to monitor pilot study progress. Injection was performed at pressures of less than 10 pounds per square inch (psi) to minimize the potential for displacement of the VOC-impacted groundwater and to allow permanganate to be distributed in the aquifer by groundwater advection. In addition, a sodium bromide tracer was added to accurately monitor subsurface distribution and injection radius of influence.

Primary monitoring events, consisting of collection of groundwater level, temperature, pH, Oxidation-Reduction Potential (ORP), alkalinity, permanganate, metals, nitrate/nitrite, VOCs, carbon dioxide, chloride, and total organic carbon, will be performed at 90 and 150 days post injection. Secondary monitoring events consisting of collection of permanganate, pH, and ORP will be performed at 30, 60, and 120 days post injection.

Performance monitoring data collected to date indicate the delivery of the oxidant was successful. Permanganate is detected in wells sidegradient and downgradient of the injection wells, indicating effective distribution. The ORP of the aquifer has changed from strongly reducing to strongly oxidizing. In addition, the bromide tracer used has persisted in the subsurface and is detected in groundwater samples.

Introduction

An ISCO pilot-scale study was performed to evaluate the effectiveness of ISCO using sodium permanganate as a potential groundwater remedial alternative for VOCs in a fractured carbonate bedrock aquifer in Eastern Iowa.

The primary objectives of the pilot study were to: (1) evaluate the ability of gravity/low-pressure injection methods to effectively deliver a sodium permanganate solution into the fractured bedrock aquifer, (2) assess the ability of the permanganate solution to effectively oxidize high concentrations of VOCs in a fractured bedrock aquifer, (3) evaluate the relative "rebound," if any, of contaminant concentrations after oxidation reactions are complete, (4) evaluate the longevity of the permanganate within the aquifer, (5) confirm the validity of the groundwater flow portion of the site conceptual model using a groundwater tracer, and (6) evaluate the effectiveness of permanganate distribution by groundwater advection.

At this time, one injection event has been completed and data collection and evaluation are ongoing.

Site Description

The facility is an active storage and distribution center for various types of industrial chemicals. It has operated as a distribution center since the early 1950s. The facility structures include a main warehouse and office building, and two smaller buildings (buildings A and B, Figure 1) situated south of the main warehouse. The southern property boundary is located approximately 500 feet from the Mississippi River.

The facility historically stored and distributed agricultural, commercial, and industrial chemical products. The northwestern corner of building A was formerly utilized as the solvent drum filling room. Gravel flooring is still evident in the filling room beneath plywood boards. Historical product storage records correlate with contaminants detected in soils and groundwater.

Site Investigation History and Regulatory Status

In 1999, a site investigation was initiated at the site and the surrounding offsite properties. Several additional phases of work were subsequently conducted under a United States Environmental Protection Agency (USEPA) Region 7 consent order.

Summary of Site Conceptual Model

The four lithologic zones present beneath the site are summarized in Table 1.

Table 1
Site Lithology

Lithologic Zone	**Approximate Extents**	**Geology**	**Hydraulic Conductivity (cm/sec)**
Unconsolidated Zone	Ground surface to top of the shallow-bedrock zone (3 to 10 feet bgs)	Silty Clay	10^{-6} - 10^{-8}
Shallow-Bedrock Zone	3 to 10 feet bgs to 50 feet bgs	Silurian-Devonian Limestone	10^{-4} - 10^{-6}
Intermediate-Bedrock Zone	50 to 250 feet bgs	Silurian-Devonian Limestone	$< 10^{-6}$
Deep-Bedrock Zone	250 feet bgs to top of Maquoketa Shale	Silurian-Devonian Limestone	No measurable flow

The uppermost groundwater surface is typically encountered at the interface between the bedrock surface and the base of the unconsolidated zone. During wet periods, the groundwater surface is within the unconsolidated zone. The groundwater flow is radially outward from the northern area of the site to the east, south, and west. Groundwater elevation maps for the site confirm that the groundwater beneath the site generally moves toward the Mississippi River. Monitoring wells near the Mississippi River indicate contaminants at or near groundwater maximum contaminant level (MCL) concentrations. In the immediate vicinity of the Mississippi River, groundwater levels are impacted by the stage of the river. During wet periods, groundwater levels in the alluvium near the Mississippi River are higher, resulting in a northerly and northwesterly groundwater flow adjacent to the river. During low water conditions, several unconsolidated zone wells are dry. Groundwater velocity for the site varies due to fractured flow conditions with a range of approximately 0.2 feet per day to 6.0 feet per day.

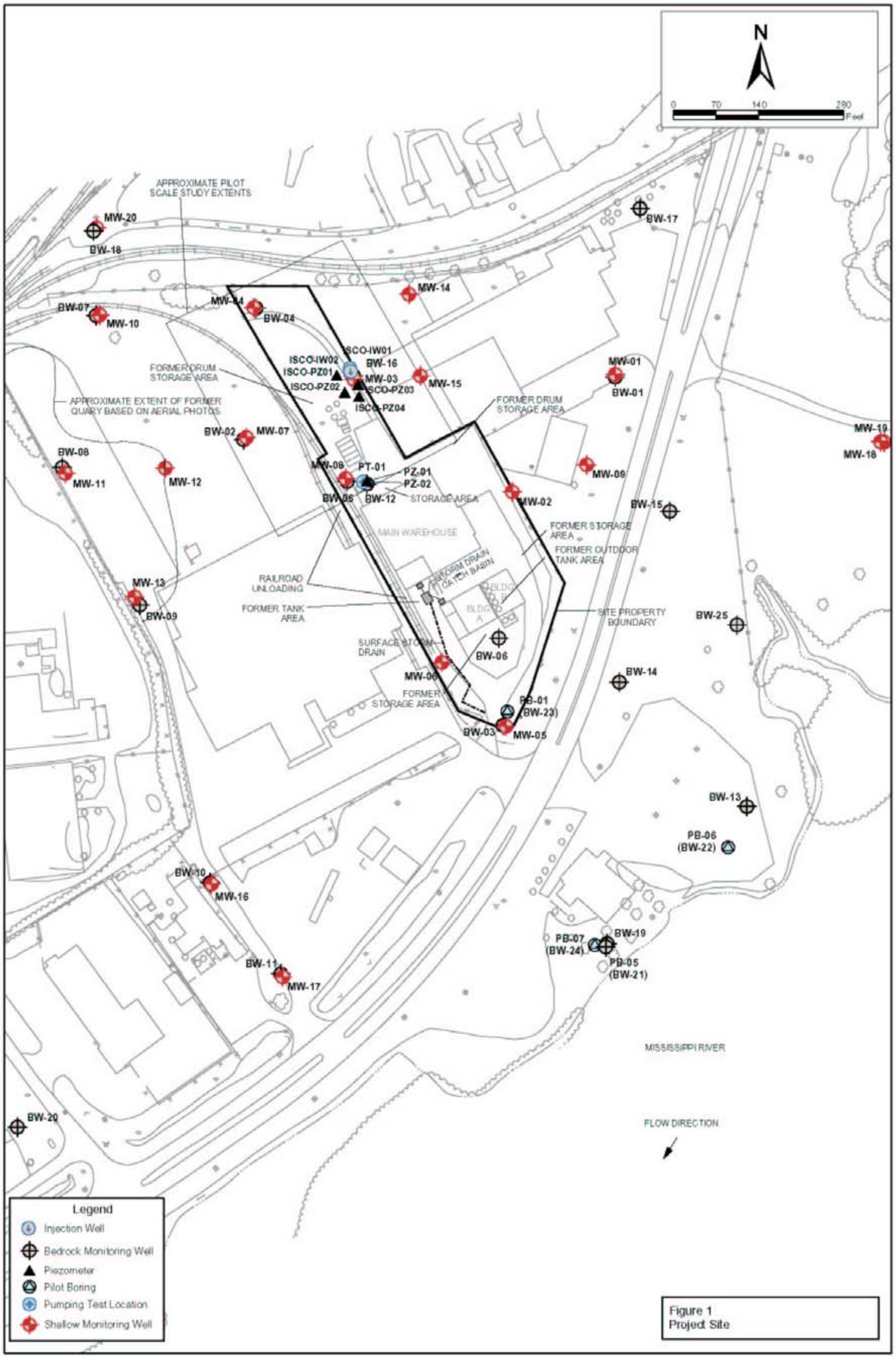

Figure 1
Project Site

The Maquoketa Shale was encountered at approximately 400 feet bgs (160 feet above mean sea level) and sampled during drilling. Based upon the results of geotechnical testing for the shale core collected, the shale has a coefficient of permeability of 7.4×10^{-10} cm/sec.

Contaminants of Concern

Numerous sources potentially contributed to conditions currently observed at the site. VOCs, primarily perchloroethylene (PCE) and related daughter products, methylene chloride, acetone, MEK, toluene, ethylbenzene, and xylenes, are the primary constituents of concern at the site.

Total VOC concentrations in soils are highest beneath the former drum filling room (13,240 mg/kg). Total VOC concentrations in the shallow-bedrock groundwater are highest in BW-03 (348 mg/L), BW-05 (308 mg/L), and BW-16 (152 mg/L).

Concentrations of VOCs detected in soil and groundwater are indicative of LNAPL and/or DNAPL. The NAPL could be either mobile (flows into a well) or residual. Extensive efforts have been made to locate and characterize potential mobile LNAPL and DNAPL source areas. Oil/water interface probes are routinely used to assess if NAPL is present (in measurable thickness) in monitoring wells; to date no mobile NAPL has been detected. During site investigation activities, a flexible liner underground technology (FLUTe™) system equipped with a NAPL reactive cover was installed in a 6-inch-diameter, 150-foot borehole in an effort to delineate potential NAPL areas. No mobile NAPL was detected using the FLUTe™ system.

The matrix porosity of the limestone bedrock has likely resulted in diffusion of NAPL into the rock matrix. As a result, it is likely that any NAPL onsite is present as isolated “globules” of residual NAPL similar in nature to that collected at BW-03.

Pilot Test Design

The ISCO pilot study was designed to focus on treatment of VOCs in the shallow-bedrock zone. Because of the complexities in the subsurface geology and potential losses due to dispersion, it is difficult to pinpoint all of the areas of heterogeneous (elevated) contamination within the pilot study area. The goal of the injection was to “flood” the shallow-zone bedrock aquifer with oxidant to maximize contact with the constituents and allow the oxidant to flow with the groundwater, following the migration pathways.

To date, an analytical standard has not been established for natural oxidant demand (NOD) studies. Based on the lack of a standard protocol, the pilot-scale study was designed to serve as the NOD study and provide qualitative data on the NOD of the aquifer. The volume of oxidant utilized for the pilot test was designed to meet an average stoichiometric oxidant ratio of 2.4 pounds per pound of VOCs amenable to oxidation (ITRC, 2001). This ratio is based on the concentration of permanganate required to oxidize individual VOCs. A NOD of 1 percent was assumed, with an effective NOD of 0.1 percent. This low, assumed NOD is consistent with anticipated conditions in a bedrock system.

The injection was designed to use gravity feed and/or low-pressure injection (10 psi or less) to deliver the permanganate to the aquifer. The low-pressure injection maximized the potential for the permanganate to mix with contaminated groundwater and to allow distribution of the permanganate by groundwater advection, dispersion, and diffusion.

Concentrations of VOCs in the pilot study area groundwater and the goal of allowing the permanganate solution to be carried with the static groundwater flow resulted in a designed injection concentration of 10 percent permanganate solution. Use of sodium permanganate was required to achieve the desired 10 percent injection concentration. The 10 percent solution would be sufficient to treat the high concentrations of VOCs, while maintaining a density greater than water. The slight density difference would allow the permanganate to follow the migration of heavier than water phases and, as a result, come into contact with any residual DNAPL in the pilot study area.

The pilot test area was selected as an area with subsurface conditions representative of site-wide conditions (based on pumping test and slug test data and groundwater conditions, field parameters, and contaminant concentrations) representative of site conditions. Based on these criteria, the area near BW-16 was selected. The pilot test area was arbitrarily set at 2,500 square feet (50 feet by 50 feet) to a depth of 35 feet bgs, roughly the depth of the shallow-bedrock zone.

Four 1-inch-diameter polyvinyl chloride (PVC) monitoring piezometers and two 2-inch diameter PVC injection wells were installed the week of March 22, 2004, using hollow-stem auger methods for the unconsolidated zone and air rotary methods in the bedrock. The piezometers were arranged in a generally radial pattern side gradient and down gradient of the two injection wells (Figure 2). The piezometers (ISCO-PZ01 through ISCO-PZ04) were screened from 10 feet bgs to 35 feet bgs. The screen length of the piezometers was designed to maximize the potential of the screened interval to intersect transmissive fractures, increasing the likelihood that the injected permanganate solution would be detected during performance monitoring. The injection wells (ISCO-IW01 and ISCO-IW02) were installed (screened intervals 20 feet bgs to 30 feet bgs and 8 feet bgs to 18 feet bgs, respectively) in an effort to equally distribute the permanganate across the shallow-bedrock aquifer, and avoid overlapping screened intervals to reduce the potential for "short-circuiting" of the permanganate solution during injection.

Pre-injection (baseline) groundwater samples were collected for the parameters in Table 2 from the four bedrock piezometers (ISCO-PZ01 through ISCO-PZ04) and four bedrock monitoring wells (BW-02, BW-04, BW-05, and BW-16) included as part of the pilot study to establish baseline conditions.

Table 2
Injection Performance Monitoring Analytical Parameters

Total Organic Carbon	1,4-dioxane	Bromide
Chloride	Alkalinity	RCRA metals (dissolved)
Nitrate	Nitrite	Carbon Dioxide
VOCs	ORP	SpC
Conductivity	Temperature	pH

Groundwater Tracer

A sodium bromide groundwater tracer was added to the permanganate solution before injection. The groundwater tracer was used to detect the presence of the injected solution prior to arrival of the permanganate. The bromide tracer would migrate with minimal retardation, while the migration of the permanganate could be influenced by reaction with organics in the aquifer and heterogeneous VOC concentrations.

Regulatory Requirements

The addition/injection of chemical oxidants to an aquifer in Iowa is regulated by the USEPA Underground Injection Control (UIC) Program. Aquifer remediation wells are categorized as Class V injection wells.

Based on the limited scale of the pilot study and the regulatory status of the site, the injection wells were allowed to operate as rule authorized under 40 CFR 144.24 without the requirement of an injection well permit.

Pilot Study Injection Activities

In response to a USEPA request, pressure transducers were installed in the four 1-inch piezometers and four nearby monitoring wells to monitor groundwater temperature and levels during injection. The transducer data would be evaluated to determine if injection activities resulted in large-scale displacement of impacted groundwater.

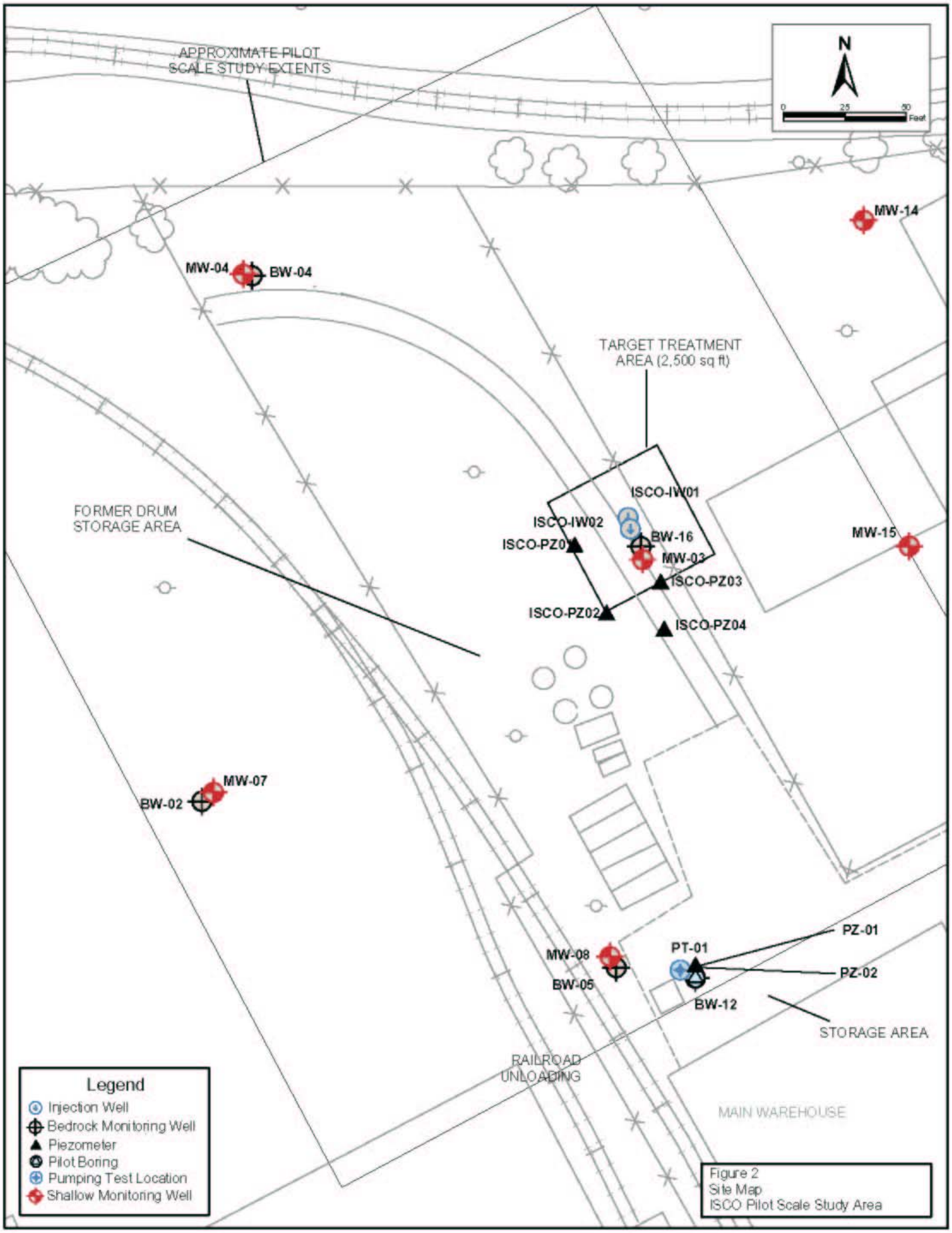

Figure 2
Site Map
ISCO Pilot Scale Study Area

Oxidant solution preparation was accomplished by adding potable water to empty 2,500-gallon poly tanks and then adding the appropriate volumes of 40 percent sodium permanganate, followed by 40 percent sodium bromide, to achieve the target injection concentrations. Injection volumes were divided with approximately 50 percent of the total volume injected into each injection well. The oxidant solution was mixed in three batches as presented in Table 3.

Table 3
ISCO Pilot Study Permanganate Injection Specifications

Injection Well ID	Injected Volume	Permanganate Concentration	Bromide Concentration	Dates of Injection
ISCO-IW01	500 gallons	2 percent	250 mg/L	3/31/2004 – 4/1/2004*
ISCO-IW02	2,500 gallons	10 percent	250 mg/L	4/5/2004 – 4/6/2004*
ISCO-IW01	1,760 gallons	10 percent	250 mg/L	4/6/2004 – 4/8/2004**

*Injection was only operated during working hours.
**Injection was operated 24 hours per day.

After mixing was completed, the discharge valve on the bottom of the poly tank was connected directly to the top of the injection well to determine if the oxidant solution could be delivered to the shallow-bedrock aquifer by gravity feed. The oxidant solution was not able to gravity feed into either injection well. As a result, the intake on the air diaphragm pump was connected to the discharge valve on the bottom of the poly tanks, and the solution was injected using the air diaphragm pump.

An initial solution of 500 gallons of 2 percent permanganate was injected into ISCO-IW01. The relatively lower concentration of the initial injection allowed troubleshooting of the injection system, with reduced health and safety concerns during system startup.

Hourly readings of flow rate and total volume were recorded from an in-line flowmeter and totalizer, in addition to visual volumetric estimates of permanganate solution remaining in the poly tanks. Hourly readings of injection rate, injection pressure, and total injection volume were recorded to confirm the injection did not exceed 10 psi. Water levels and groundwater temperatures during injection activities were measured by pressure transducers installed in ISCO-PZ01, ISCO-PZ02, ISCO-PZ03, ISCO-PZ04, BW-02, BW-04, BW-05, and BW-16.

Injection Observations

Injection using gravity feed was not sustainable at ISCO-IW01 or ISCO-IW02. Average injection rates based on volumetric estimates varied between ISCO-IW01 and ISCO-IW02. The average flow rate for ISCO-IW01 was approximately 0.5 gallon per minute, while the injection flow rate for ISCO-IW02 was 2.6 gallons per minute. The lower injection rate for ISCO-IW01 is likely due to the heterogeneous nature of the fractured bedrock in the shallow-bedrock zone. ISCO-IW02 is screened shallower in the aquifer where the bedrock is more weathered, and more highly fractured based on rock core logs for the area.

After approximately 4 hours of injection into ISCO-IW01, permanganate solution was observed flowing out of the well casing of BW-16, approximately 15 feet south of ISCO-IW01. To prevent continued discharge of permanganate from BW-16, the pressure transducer was removed and the pressure cap was reinstalled. Five minutes after sealing BW-16, permanganate solution was observed flowing out the top of the well casing for ISCO-PZ01, approximately 25 feet west of ISCO-IW01. Again, the pressure transducer was removed and the pressure cap reinstalled to prevent additional discharge.

After approximately 3 hours of injection into ISCO-IW02, permanganate solution was observed flowing out of the well casing of ISCO-PZ03. In response, the pressure transducer was removed and the pressure cap was replaced, allowing injection to continue. During injection at ISCO-IW02, small volumes (less than 2 gallons total) of permanganate were observed migrating to the ground surface through the soil near ISCO-IW02. Injection rates were reduced from approximately 4 gallons per minute to 2.5 gallons per minute, and the migration of permanganate solution through the soil stopped.

Increases in groundwater elevation were recorded during injection by pressure transducers installed in ISCO-PZ01 through ISCO-PZ04 and BW-16. Transducers installed in BW-16 and ISCO-PZ01 were removed during initial injection into ISCO-IW01, so no evaluation of response to injection into ISCO-IW02 was possible for these locations. Increases in groundwater levels during injection into ISCO-IW01 were recorded at BW-16, ISCO-PZ01, and ISCO-PZ03. Increases in groundwater levels during injection into ISCO-IW02 were recorded at ISCO-PZ03 and ISCO-PZ04. No water level increases were recorded at perimeter wells BW-02, BW-04, or BW-05.

Results and Conclusions

Performance monitoring parameters are collected from BW-02, BW-04, BW-05, BW-16, and ISCO-PZ01 through ISCO-PZ04 to monitor aquifer conditions and response to the pilot study. Performance monitoring is divided into primary and secondary monitoring events. Primary monitoring events are performed at 90 days and 150 days post-injection and include collection of groundwater samples for the parameters in Table 2. April 2004 data represent pre-injection (background) conditions.

Secondary monitoring events are performed every 30 days (May 2004, June 2004, and August 2004), and include collection of bromide samples and field parameters including ORP, specific conductance, conductivity, temperature, and pH.

Primary monitoring events are scheduled for July 2004 and September 2004. To date, two secondary and one primary monitoring event have been completed; however, analytical data for the primary monitoring event were not available for inclusion in this paper. Data from secondary monitoring events and field parameters from the July 2004 primary monitoring event are summarized in Table 4.

Table 4
Post-Injection Monitoring Field Parameters

	ISCO-PZ01				**ISCO-PZ02**			
	Apr-04	May-04	Jun-04	Jul-04	Apr-04	May-04	Jun-04	Jul-04
Temp (C)	10.31	13.67	15.44	15.02	11.27	13.02	15.05	15.09
SpC (us/cm)	1,179	19,137	17,368	15,250	1,717	1,558	1,735	1,690
Conductivity (us/cm)	849	15,010	14,198	12,346	1,267	1,202	1,405	1,370
DO (%)	20.4	NC	NC	NC	42.8	NC	NC	NC
DO (mg/L)	2.08	NC	NC	NC	4.56	NC	NC	NC
pH	7.15	7.72	7.36	7.36	7.09	6.79	6.45	6.52
ORP (mV)	-78.3	663.6	524.9	623.7	69.8	371.2	199.6	-65.5
Permanganate (mg/L)	NA	16,605	17,450	13,100	NA	0.0	0.0	0.0
Bromide (mg/L)	<0.38	114	94.9	NA	<0.44	6.2	7.70	NA

	ISCO-PZ03				**ISCO-PZ04**			
	Apr-04	May-04	Jun-04	Jul-04	Apr-04	May-04	Jun-04	Jul-04
Temp (C)	10.13	13.65	17.07	15.77	11.45	12.98	16.11	15.28
SpC (us/cm)	1,023	16,873	11,537	9,173	1,012	1,289	1,212	1,830
Conductivity (us/cm)	732	13,214	9,790	7,552	747	991	1,212	1,455
DO (%)	13.8	NC	NC	NC	42.0	NC	NC	NC
DO (mg/L)	1.47	NC	NC	NC	4.57	NC	NC	NC
pH	6.67	7.57	6.96	7.04	7.06	6.63	6.54	6.67
ORP (mV)	35.6	712.8	600.1	630.1	1.8	581.0	570.7	641.6
Permanganate (mg/L)	NA	18,525	8,500	5,500	NA	111.28	130.00	950
Bromide (mg/L)	<0.5	120	85	NA	<0.39	<50	<50	NA

	BW-02				**BW-04**			
	Apr-04	May-04	Jun-04	Jul-04	Apr-04	May-04	Jun-04	Jul-04
Temp (C)	7.64		14.30	15.68	10.38	11.75	15.35	15.21
SpC (us/cm)	1,006		1,047	1,046	528	544	549	540
Conductivity (us/cm)	668		833	860	380	406	448	438
DO (%)	14.0	Not	NC	NC	16.1	NC	NC	NC
DO (mg/L)	1.56	Sampled	NC	NC	1.80	NC	NC	NC
pH	7.24		5.87	6.80	7.50	7.84	7.50	7.62
ORP (mV)	-36.3		350.4	-86.6	-85.8	-135.6	-186.5	-164.3
Permanganate (mg/L)	NA		0.0	0.0	NA	0.0	0.0	0.0
Bromide (mg/L)	<0.40		<0.23	NA	<0.44	<0.48	<0.40	NA

	BW-05				**BW-16**			
	Apr-04	May-04	Jun-04	Jul-04	Apr-04	May-04	Jun-04	Jul-04
Temp (C)	7.75	11.78	15.28	16.98	11.42	13.87	16.75	16.19
SpC (us/cm)	1,569	1,763	1,741	1,719	1,157	27,530	17,325	12,748
Conductivity (us/cm)	1,054	1,319	1,416	1,455	857	21,720	14,628	16,604
DO (%)	14.9	NC	NC	NC	26.2	NC	NC	NC
DO (mg/L)	1.76	NC	NC	NC	2.60	NC	NC	NC
pH	6.68	6.74	6.26	6.37	6.77	6.52	6.04	6.19
ORP (mV)	-92.0	-56.2	-90.0	-106.7	-66.2	753.6	657.9	711.8
Permanganate (mg/L)	NA	0.0	0.0	0.0	NA	25,450	20,500	14,900
Bromide (mg/L)	<0.38	<50	<0.31	NA	<0.36	123	105	NA

NC indicates parameter not collected.
NA indicates data not available at time of printing

Groundwater sample collection is accomplished using low-flow sampling methods. No dissolved oxygen (DO) readings were collected post-injection because the presence of high permanganate concentrations will damage the DO membrane and the DO probe.

Pre-injection (April 2004) conditions are indicative of a reducing environment with low DO and ORP values. The post-injection area of elevated ORP readings extends approximately 50 feet south of the injection points to

ISCO-PZ04. Bromide concentrations at ISCO-PZ04 were below detection limits in May 2004. Groundwater samples collected from ISCO-PZ03 indicate that high concentrations of permanganate remain approximately 25 feet south of the injection points.

To the west (sidegradient to upgradient) of the injection wells, high ORP readings correlate with high concentrations of permanganate (over 15,000 mg/L) in ISCO-PZ01. ORP readings have also increased in BW-02 from –36.3 mV prior to injection to 350.4 mV in June 2004. No permanganate was detected in groundwater samples collected from BW-02 using spectrophotometry. Permanganate concentrations were measured in the field using a portable spectrophotometer. Prior to use, the spectrophotometer was calibrated with a laboratory standard permanganate solution. The spectrophotometer allowed measurement of permanganate concentrations up to 50 mg/L. Permanganate concentrations over 50 mg/L required dilution prior to analysis. The dark purple color of groundwater samples containing over 50 mg/L of permanganate prevents sufficient light from passing through the sample, resulting in erroneous measurements.

Groundwater samples collected from ISCO-PZ02, southwest of the injection area, show elevated ORP readings of 371.2 mV in May and 199.6 mV in June. Bromide concentrations at ISCO-PZ02 were 6.2 mg/L and 7.7 mg/L in May 2004 and June 2004, respectively.

Northern and southern “background” wells BW-04 and BW-05, respectively, continue to show conditions similar to pre-injection conditions. ORPs remain strongly negative and no permanganate or bromide has been detected at either location.

High concentrations of permanganate in groundwater samples have limited the collection of groundwater samples for laboratory analysis. Potential reactions between permanganate and sample preservatives and damage to laboratory instruments from the permanganate result in elevated detection limits, potential health and safety issues, and, in some cases, the elimination of sample collection. Further evaluation of alternative preservatives and data requirements will be performed to determine an effective method for sample collection and preservation.

Distribution of the injected solution was achieved up to 45 feet from the injection points through 2-inch PVC injection wells with 10-foot screened intervals. The extents of permanganate to the southwest and south of the pilot study area are well defined by ISCO-PZ02 and ISCO-PZ04. The eastern and western extents of the permanganate are beyond the initial boundaries of the monitoring network. Groundwater flow in the injection area is likely to the southeast. Addition of a shallow-bedrock well to the east of the injection area would allow monitoring of the downgradient extents of the permanganate. In addition, an additional monitoring well to the east of the injection area would allow a more detailed evaluation of permanganate solution migration by groundwater transport. Appropriate locations and data quality objectives are being evaluated before installation of additional monitoring points.

Pre-injection concentrations of bromide in the shallow-bedrock aquifer were below analytical detection limits. The sodium bromide tracer has allowed evaluation of permanganate migration rates relative to the bromide tracer, and comparison of groundwater flow paths in the shallow-bedrock aquifer against the site conceptual model. Bromide has been detected in pilot study monitoring wells to the south and west of the injection area. The lack of bromide in BW-02, BW-04, and BW-05 confirms the injection of the permanganate solution did not result in large-scale displacement of groundwater in the pilot study area.

The objective of allowing the oxidant to be carried through the aquifer by movement of groundwater required the use of an oxidant capable of persisting in the subsurface after injection. Performance monitoring indicates permanganate has persisted in the subsurface for more than 90 days, and concentrations of permanganate near the injection wells remain at nearly 2 percent.

Path Forward

Performance monitoring for the ongoing pilot study will continue, and an additional monitoring piezometer east of the injection area will be added to supplement data on test effectiveness. The pilot-scale study will be expanded at the site based on the success of the initial injection. Additional injection well nests will be added on the northern and southern portions of the site. Additional permanganate will be injected and monitored with the same goals established for the initial injection. The pilot study will be slowly expanded in phases with target treatment areas similar in size to the initial 2,500 square feet to a depth of approximately 35 feet bgs. Implementation in phases allows expansion of the treatment areas only as necessary based on real-time data collection.

If pilot study results continue to show favorable results, full-scale implementation of ISCO will be considered as part of a comprehensive site remedial alternative. Source area soils would likely be addressed. Concurrently, permanganate would be added to the shallow bedrock and unconsolidated zone. The high concentrations of VOCs in shallow-bedrock groundwater would result in recontamination of cleaned soils during periods of high groundwater elevations. In addition, continued leaching from source area soils could recontaminate groundwater remediated by ISCO. By using ISCO combined with source area soil treatment, the permanganate will migrate into site soils during periods of high groundwater elevations treating any remaining areas of low contaminant concentrations. In addition, the elimination of contaminants leaching into groundwater will minimize the amount of permanganate required to effectively reduce concentrations of contaminants in groundwater.

It is anticipated that periodic reinjection of permanganate will be required due to diffusion of contaminants out of the bedrock matrix (rebound), complete reduction of the permanganate by NOD in soils, and dilution of injected permanganate by infiltration and floods. Conditions mandating reinjection will be evaluated before any full-scale implementation. The need for reinjection will be determined by several factors, including: (1) contaminant concentration rebound, (2) residual permanganate concentrations, (3) downgradient groundwater conditions (pH, ORP, DO, contaminant concentrations), and (4) periodic groundwater monitoring events. This flexible approach, based on multiple real-time site conditions, will allow effective source removal/mass reduction, while allowing proven natural processes (natural attenuation) to effectively remediate low-concentration downgradient areas. Periodic groundwater monitoring events will effectively measure plume stabilization/reduction with minimal operation and maintenance costs, compared to pump and treat system operation costs.

Reference

In Situ Chemical Oxidation Work Team, 2001, *Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater,* Interstate Technology and Regulatory Cooperation Work Group.

Biographical Sketches

Paul D. Rohde, CH2M HILL, 135 South 84th Street, Suite 325; Milwaukee, WI 53214, phone: 414-847-0376, fax: 414-272-4008, prohde@ch2m.com. Mr. Rohde is a hydrogeologist at CH2M HILL with 5 years experience working on site investigation and remediation projects under CERCLA, RCRA, and state cleanup programs. His expertise includes fractured bedrock site investigation, hydrogeologic site characterization, groundwater remedial technologies, chlorinated solvents, and environmental baseline assessment.

Cynthia R. Butler, P.E., CH2M HILL, 825 NE Multnomah, Suite 1300, Portland, OR 97232, phone: 503-872-4441, fax: 503-736-2001, cbutler@ch2m.com. Ms. Butler is a project manager at CH2M HILL with 9+ years of experience working on site investigation and remediation projects under both RCRA corrective action and state-led voluntary cleanup programs. Her expertise includes chlorinated solvents, creosote, dioxins, diesel, organochlorine pesticides, and phenoxy herbicides.