

**In Situ Redox Manipulation Pilot Field Test:
Remedial Design Support for ISRM Barrier
Deployment**

**Frontier Hard Chrome Superfund Site
Vancouver, WA**

December, 2002

Vince R. Vermeul
Mark D. Williams
Jim E. Szecsody
John S. Fruchter

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy
Richland, WA 99352

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Executive Summary

This letter report documents preliminary results from the In Situ Redox Manipulation (ISRM) pilot field tests for the treatment of hexavalent chromium in the groundwater at the Frontier Hard Chrome (FHC) site, Vancouver, Washington. The ISRM technology involves the creation of a permeable treatment zone downstream of a contaminant plume or contaminant source through injection of a chemical reducing agent to alter the redox potential of aquifer fluids and sediments. Injected reagents create the zone through reactions that reduce iron naturally present in aquifer sediments from Fe(III) to Fe(II). Following the creation of the ISRM treatment zone, hexavalent chromium contaminated groundwater will flow into and through the treatment zone under natural groundwater flow conditions. As the dissolved hexavalent chromium (in the form of highly soluble and mobile chromate anion, CrO_4^{2-}) enters the reducing environment, it will react with the ferrous iron in the treatment zone and be reduced to the trivalent form which readily hydrolyzes and precipitates as $\text{Cr}(\text{OH})_3(\text{s})$.

The objective of the ISRM pilot test was to determine the field-scale feasibility of this innovative remediation technology for the treatment of the hexavalent chromium contamination in the groundwater at FHC. Bench-scale analysis of sediment from the site were conducted with favorable results and subsequent field-scale testing was conducted to determine the feasibility at a larger scale in the complex hydrogeologic and geochemical conditions of the subsurface. Data from the ISRM pilot test will be used to determine the feasibility of, and develop the remedial design for, a full-scale ISRM barrier at this location.

The ISRM pilot test site well network, which was designed to refine the hydrogeologic conceptual model of the site and provide the wells required to monitor the treatment zone emplacement, was comprised of two centrally located injection wells surrounded by 11 monitoring wells. During and immediately following installation of this well network, site specific characterization activities were conducted to determine the hydrogeologic, geochemical, and hydrologic parameters required to develop the ISRM treatments zone emplacement design. The hydrogeology encountered beneath the ISRM pilot test site indicated that the A aquifer zone contained far more heterogeneity than was accounted for in the original hydrogeologic conceptual model of the site. The refined conceptual model of the A aquifer consists of, in descending order, a silty sandy gravel layer ~5 ft thick (referred to here as the A1 zone), another silty sandy gravel layer ~8 ft thick (referred to here as the A2 zone) that has an estimated hydraulic conductivity value an order of magnitude higher than that for the A1 zone, and a sandy gravel layer ~ 5 ft thick that was estimated to be approximately another order of magnitude higher in hydraulic conductivity (A3 zone). The A aquifer at this location extended from approximately 22 ft to 40 ft below ground surface.

During the ISRM pilot test, a total volume of 44,000 gallons of reagent was injected into well INJ-2 at a rate of 40 gpm for 18.3 hours. The average reagent concentration for the pilot dithionite injection test was 0.1 M sodium dithionite with a 0.4 M potassium carbonate pH buffer. Results from the pilot dithionite injection test, in conjunction with results from the tracer injection test, showed that the site has a very high degree of variability in hydraulic properties controlling the direction and extent of reagent transport and treatment capacity distribution during the

emplacement process. This type of spatial variability likely will limit the potential injection well spacing because a conservative approach will be required that provides the highest likelihood of constructing a continuous barrier (i.e., minimizes the potential for holes in the barrier). Pilot-scale testing activities have demonstrated the need for detailed characterization of hydrogeologic conditions and contaminant distribution along the length of the barrier. This information will be required to determine how much conditions change across the proposed barrier length relative to the pilot test site and how this will affect injection designs for full-scale deployment.

Preliminary performance assessment of the ISRM pilot test site is based on comparison of Cr(VI) concentrations within the treatment zone following emplacement of the reduced zone with pre-treatment baseline conditions. These preliminary Cr(VI) performance data look promising. Hexavalent chromium concentrations have been reduced from as high as 4,500 $\mu\text{g/L}$ to below detection limits in all monitoring wells within the established treatment zone. Due to project constraints, additional interpretation and reporting of performance measures (e.g., DO, ORP, trace metals concentrations) was not completed for inclusion in this letter report.

TABLE OF CONTENTS

	<u>Page Number</u>
1.0 Introduction	1
1.1 Technology Description	6
1.2 Field Test Objective	8
1.3 Report Organization	9
2.0 Pilot Test Site Characterization	10
2.1 Well Installation	10
2.2 Hydrogeologic Characterization	13
2.3 Geochemical Characterization	17
2.4 Hydrologic Characterization	17
2.5 Baseline Groundwater Chemistry	21
3.0 Pilot Test Site Setup	23
3.1 Site Utilities	23
3.2 Monitoring Equipment	24
3.3 Analytical Measurements	25
3.4 Injection and Withdrawal Equipment	26
3.5 Description of Equipment Integration/Operation	28
4.0 Bromide Tracer Test	29
4.1 Tracer Test Objectives	29
4.2 Tracer Test Description	29
4.3 Tracer Test Results and Discussion	30
5.0 ISRM Treatment Zone Emplacement	34
5.1 Emplacement Strategy	34
5.2 Emplacement Description	38
5.3 Emplacement Results and Discussion	39
6.0 Preliminary Performance Assessment	44
7.0 References	47
Appendix A: Geologic Logs and Well Installation Reports	
Appendix B: Electromagnetic Borehole Flow Meter Testing	
Appendix C: Tracer Test Breakthrough Curves	
Appendix D: Dithionite Injection Breakthrough Curves	

1.0 Introduction

This letter report documents preliminary results from the In Situ Redox Manipulation (ISRM) pilot field tests for the treatment of hexavalent chromium in the groundwater at the Frontier Hard Chrome (FHC) site, Vancouver, Washington. The FHC site is located in the southwestern part of the State of Washington, in the city of Vancouver. The site is approximately one-half mile north of the Columbia River and covers about one-half acre. Chrome plating operations occurred at the FHC site for approximately 25 years between 1958 and 1982. FHC, which operated at the site between 1970 to 1982, discharged process waste-waters containing hexavalent chromium directly to an on-site dry well.

In 1982, Washington State Department of Ecology (Ecology) determined that FHC was violating Washington State Dangerous Waste Regulations for disposal of hazardous waste. At that time, chromium concentrations greater than twice the state groundwater cleanup standard of 50 ug/L (MTCA A) were detected in groundwater samples from an industrial well located at the FMC site approximately 0.5 miles southwest of the site. FHC went out of business shortly after Ecology identified the violation. In December 1982, the site was proposed for inclusion on the National Priorities List (NPL) under CERCLA. The site was added to the NPL in September, 1983.

Releases from FHC operations contaminated groundwater with reported chromium concentrations as high as 300,000 ug/L. At the time the contaminated groundwater was first detected, a groundwater plume exceeding Washington State groundwater cleanup standards (50 ug/L) extended approximately 1600 ft southwest from the facility. The July 1988 ROD for the groundwater operable unit called for extraction of groundwater from the area of greatest contamination (levels of chromium in excess of 50,000 ug/L) via extraction wells, and treatment of extracted groundwater. Groundwater monitoring since initial discovery has shown that the plume has receded. Monitoring in 2000 indicated that the plume exceeding state groundwater cleanup standards extends approximately 1000 feet south of the site. The change in overall plume size, and the shift in groundwater flow from the site in a southwesterly direction to a more southerly direction is largely due to the discontinued pumping of three large industrial supply wells located at the FMC facility. With the influence of these wells eliminated, the plume is conforming to natural groundwater flow. While monitoring indicates that the plume is receding, it also shows that concentrations beneath the FHC site, or the plume "hot spot" area, defined in this plan by chromium concentrations exceeding 5,000 ug/L, have remained consistently high over time.

Concentrations of total chromium in surface soils collected for the Remedial Investigation were found as high as 5,200 mg/kg while recent surface soil samples revealed concentrations of hexavalent chromium near the FHC building as high as 42 mg/kg. Subsurface concentrations for total and hexavalent chromium have been noted as high as 31,800 mg/kg and 7,506 mg/kg respectively. Contaminated subsurface soils extend beneath the neighboring Richardson Metal Works building. The December, 1987 ROD for the soils/source control operable unit called for removal, stabilization and replacement of 7400 cubic yards of soil - or all soils with concentrations greater than 550 mg/kg total chromium (this number was based on a site specific leachate test for protection of groundwater).

EPA issued separate RODs for the soils/source control operable unit (December 1987) and the groundwater operable unit (July 1988). Evaluation of these proposed remedies by EPA after the RODs were issued revealed the soils remedy to be ineffective. Groundwater monitoring conducted after the ROD was issued indicated that the contaminated groundwater plume was decreasing in size as down-gradient industrial supply wells located at FMC were taken off line. As the immediate threat of further down-gradient migration of the plume appeared to be in decline, and as local government controls were in place preventing installation of new wells in the aquifer, EPA also began to reevaluate the need for pump and treat as the most appropriate solution for groundwater cleanup. Since that time, EPA has continued to monitor groundwater and soils, and

evaluate new, innovative cleanup technologies to address the persistently high concentrations in soils and groundwater at the FHC site.

In October, 1994 Ecology conducted an interim removal action of chromium contaminated soil on the property adjacent to and east of the FHC site. Approximately 160 cubic yards of soil were removed and disposed of allowing for redevelopment of the property. With the exception of this interim removal action, no active cleanup has taken place. While monitoring is ongoing, no active steps have been taken to control or remediate contaminated groundwater, and no actions have been taken to deal with contaminated soils on the FHC and adjacent Richardson Metal Works properties which continue to act as a source of contamination to the groundwater resource. In May, 2000, EPA finalized a Focused Feasibility Study which identified and evaluated several new and innovative technologies for addressing the problems at the site.

In June, 2001, EPA released a Proposed Plan for ROD Amendment addressing both the groundwater and soils at the site. The preferred remedy calls for the reduction of hexavalent chromium in soils and groundwater to trivalent chromium. The preferred alternative in the Proposed Plan includes in-situ treatment of source area groundwater, in conjunction with an in-situ, down-gradient treatment barrier (In-Situ Redox Manipulation, or ISRM). The preferred methodology for delivering reductant to both soils and groundwater for in-situ treatment in the soils source area and the plume hot spot is augering/injection. The ISRM Treatment Barrier would be installed on the down-gradient edge of the groundwater hot spot using injection wells (Figure 1.1). Groundwater contaminated above state cleanup standards which is down-gradient of the ISRM Treatment Barrier would be left to disperse and dilute. The combination of these alternatives would allow for the treatment of groundwater and soils in the soils source area (soils exceeding 19 mg/kg hexavalent chromium) and the groundwater plume "hot spot" at the same time (groundwater exceeding 5,000 ug/L) using the same reductant and the same methodology (auguring). Installation of an ISRM barrier provides additional long term protection of groundwater as well as protection of down-gradient groundwater during augering/injection of reductant into source area soils and the plume "hot spot" area. This alternative provides for effective treatment of all soils and groundwater in

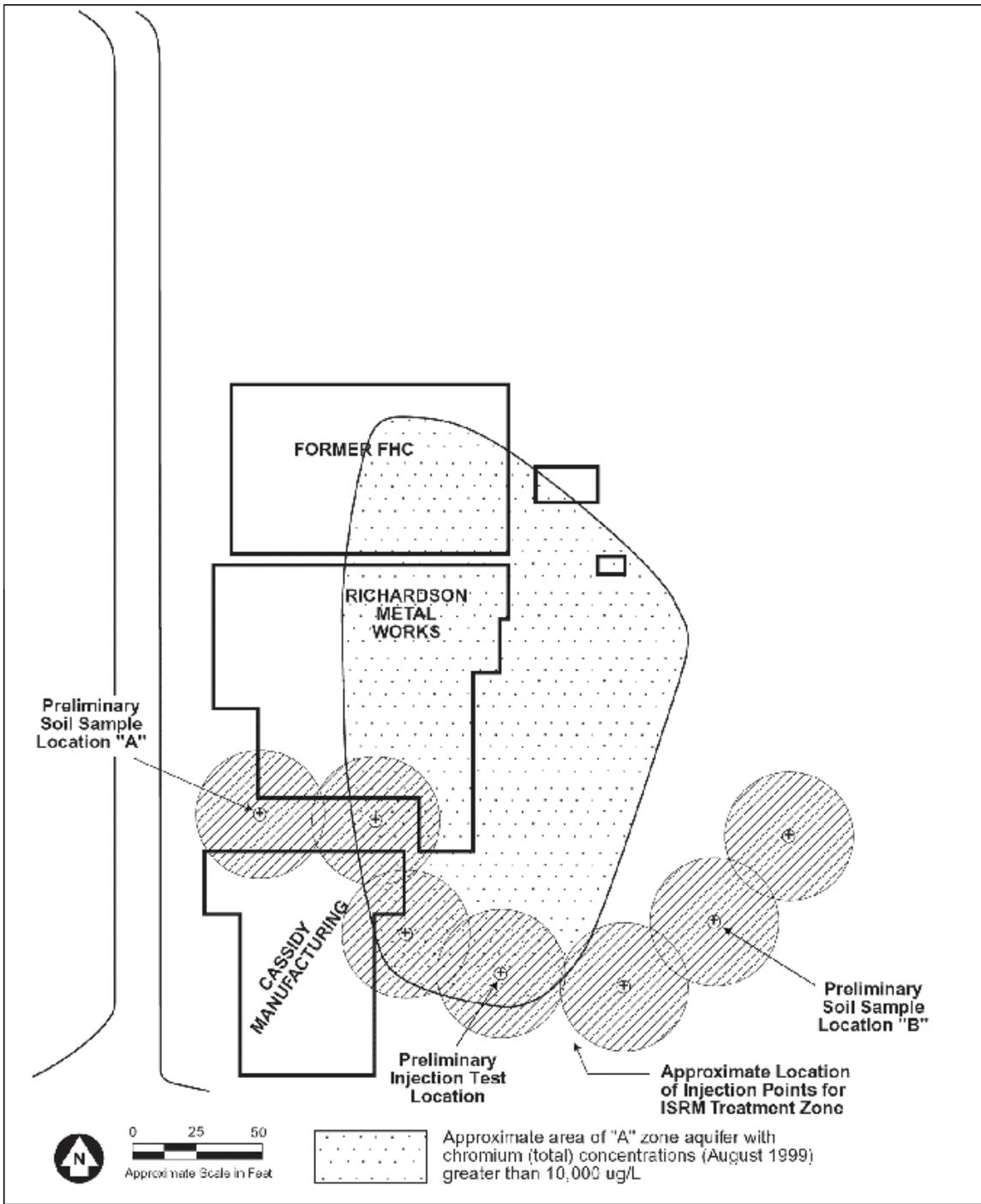


Figure 2
ISRM Treatment Barrier

02-0160 Fig2.ai

Figure 1.1. Site Map Showing the Approximate Locations of the Source Term Shallow Soil Mixing Area and the ISRM Barrier Location

source areas, and a long-term treatment barrier for any residual contaminant leaching, should it occur.

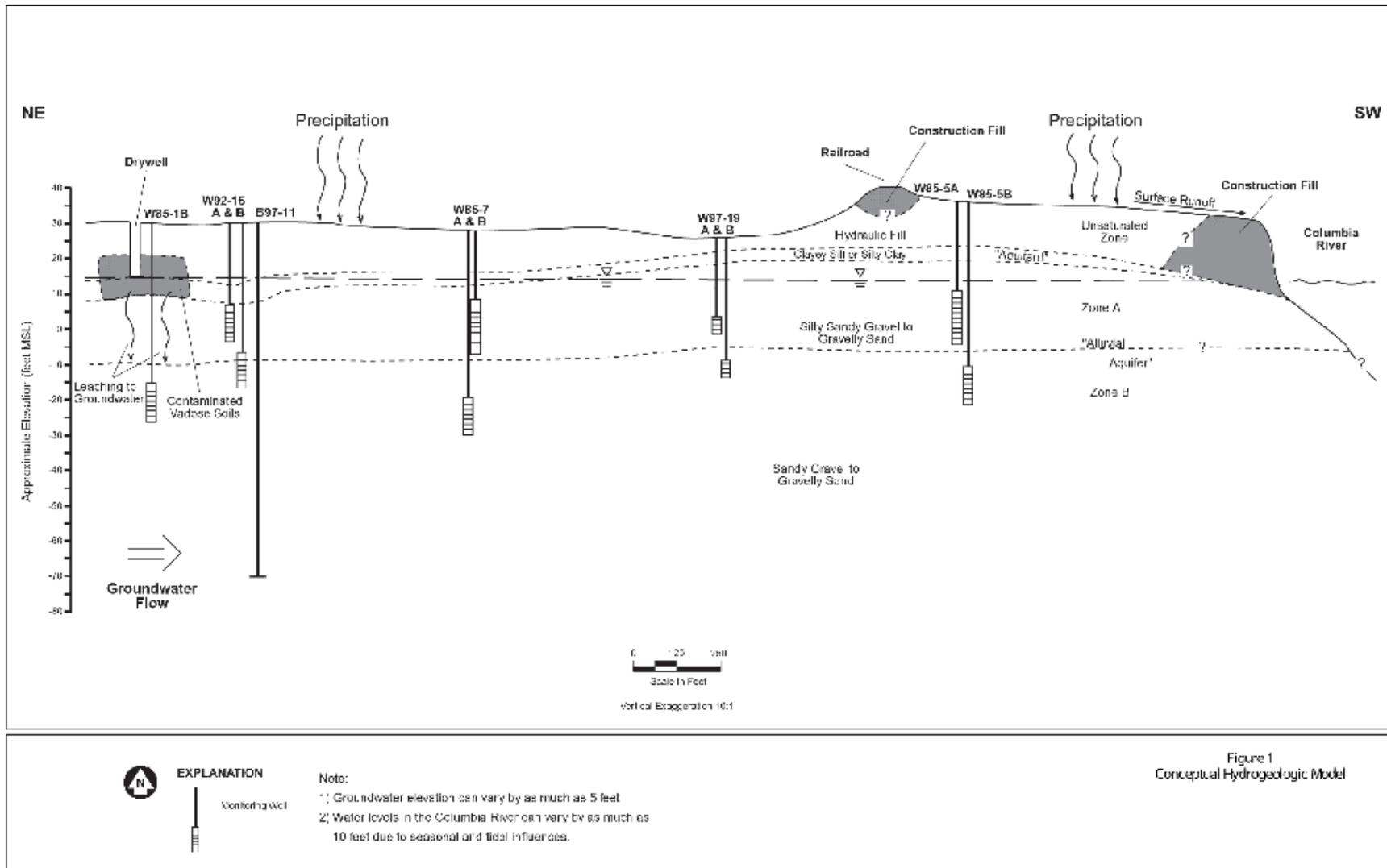
Shallow groundwater in the FHC area occurs within a complex, heterogeneous alluvial aquifer system that is hydraulically connected to the Columbia River. In general, the alluvial aquifer system exhibits both quasi-confined and confined characteristics. This semiconfined condition is due, in part, to a low-permeability clayey silt unit that directly overlies the alluvial aquifer and to permeability contrasts within the alluvial aquifer.

The site hydrogeology consists of 15 to 20 feet of random fill and silty sand, which is largely unsaturated, a 5 to 10 feet thick upper confining bed of clayey silt, and a heterogeneous anisotropic alluvial aquifer system that may be as thick as 70 feet beneath the site. Localized zones of perched groundwater are present above the top of the clayey silt within the fill materials. Figure 1.2 is a conceptual diagram of the general hydrostratigraphy inferred to be locally present in the Frontier Hard Chrome site area.

The uppermost hydrogeologic unit consists of perched groundwater in the fill unit. The fill unit is generally unsaturated but locally perched water is present. Groundwater in the perched aquifer is generally recharged from precipitation by direct infiltration and stormwater dry wells and roof drains. Separating the fill unit from the alluvial unit is the 1 to 10 feet thick confining unit.

Underlying the clayey silt unit is the alluvial aquifer. The alluvial aquifer is a sand and gravel layer beginning 15 to 20 feet below the ground surface. The upper portion of the alluvial unit has been subdivided into two water-bearing zones based on the apparent presence of a discontinuous silty sand or sandy silt zone present at depth of 25 to 35 feet bgs. The upper zone has been referred to as the "A" zone or "A" aquifer, and the lower zone has been designated as the "B" zone or "B" aquifer. The silt zone when present is generally from 1 to 3 feet thick. The silt appears to be discontinuous. Although this silt layer may act locally as a confining unit, most evidence suggests that this unit does not act as an areally extensive hydraulic barrier within the alluvial aquifer. Variations from this site-scale hydrogeologic conceptual model for the ISRM pilot test site, based on site specific characterization data collected during pilot test field activities, are discussed in Section 2.2.

The potentiometric surface is relatively flat across the inactive floodplain on which the Frontier Hard Chrome site is located. Based on previous hydrologic studies, hydraulic conductivity of the alluvial aquifer, which is highly variable, ranges from ~ 3 to 300 ft/d as measured by slug tests, grain size analysis and pumping tests. Groundwater flow is approximately 0.5 to 5 feet per day towards the river. The average hydraulic gradient is 0.00015 ft/ft.



06-16-10, Fig 1.1

Figure 1.2. Site Conceptual Hydrogeologic Model

1.1 Technology Description

The In Situ Redox Manipulation (ISRM) approach involves the creation of a permeable treatment zone downstream of a contaminant plume or contaminant source through injection of a chemical reducing agent to alter the redox potential of aquifer fluids and sediments (Fruchter et al., 2000, 1994; Vermeul et al., 2002). Redox-sensitive contaminants migrating through this treatment zone are immobilized (metals) or destroyed (organic solvents). Injected reagents create the zone through reactions that reduce iron naturally present in aquifer sediments from Fe(III) to Fe(II). Use of standard wells for treatment zone creation allows treatment of contaminants too deep for conventional trench-and-fill technologies. A conceptual diagram of the ISRM technology is shown in Figure 1.3.

This technology has been successfully demonstrated in two field tests at the Hanford Site in Washington State for the remediation of hexavalent chromium in the groundwater (Fruchter et al., 2000, 1996; Williams et al., 2000). The reducing agent used in these field and laboratory tests is sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$). Sodium dithionite is a strong reducing agent and it possesses a number of desirable characteristics for this type of application, including instability in the natural environment (~ days) with reaction and degradation products which ultimately oxidize to sulfate. A potassium carbonate/bicarbonate pH buffer is also added to the injection solution to enhance the stability of dithionite during the reduction of available iron.

Following the creation of the ISRM treatment zone, hexavalent chromium contaminated groundwater will flow into and through the treatment zone at the natural groundwater velocity. As the dissolved hexavalent chromium (in the form of highly soluble and mobile chromate anion, CrO_4^{2-}) enters the reducing environment, it will react with the ferrous iron in the treatment zone and be reduced to the trivalent form. Trivalent chromium is much less toxic and mobile in the environment. Trivalent chromium in solution readily hydrolyzes and precipitates as $\text{Cr}(\text{OH})_3(\text{s})$ (Rai et al., 1989). When trivalent chromium is precipitated in soils containing ferric iron, solid solutions with ferric iron also form, $(\text{Cr,Fe})(\text{OH})_3(\text{s})$. A more detailed review and discussion of these processes are contained in Fruchter et al., 2000.

Potential secondary effects associated with the ISRM technology include metals mobilization, residuals concentrations, hydraulic performance (i.e., aquifer plugging), and dissolved oxygen depletion. In previous bench- and field-scale demonstrations of ISRM, none of these effects were shown to exceed technical or regulatory limits. During development of the ISRM technology, one of the primary concerns was the potential for releasing unwanted constituents as the chemical treatment zone is formed. For example, as the reductive environment is formed, otherwise stable minerals or hydroxides can be broken down to release metals such as arsenic and manganese. The ISRM technology has been field-tested at several sites, including a proof-of-principle test at the Hanford 100-H Area for removing chromium from groundwater (Fruchter et al. 2000), a treatability test at the Hanford 100-D Area

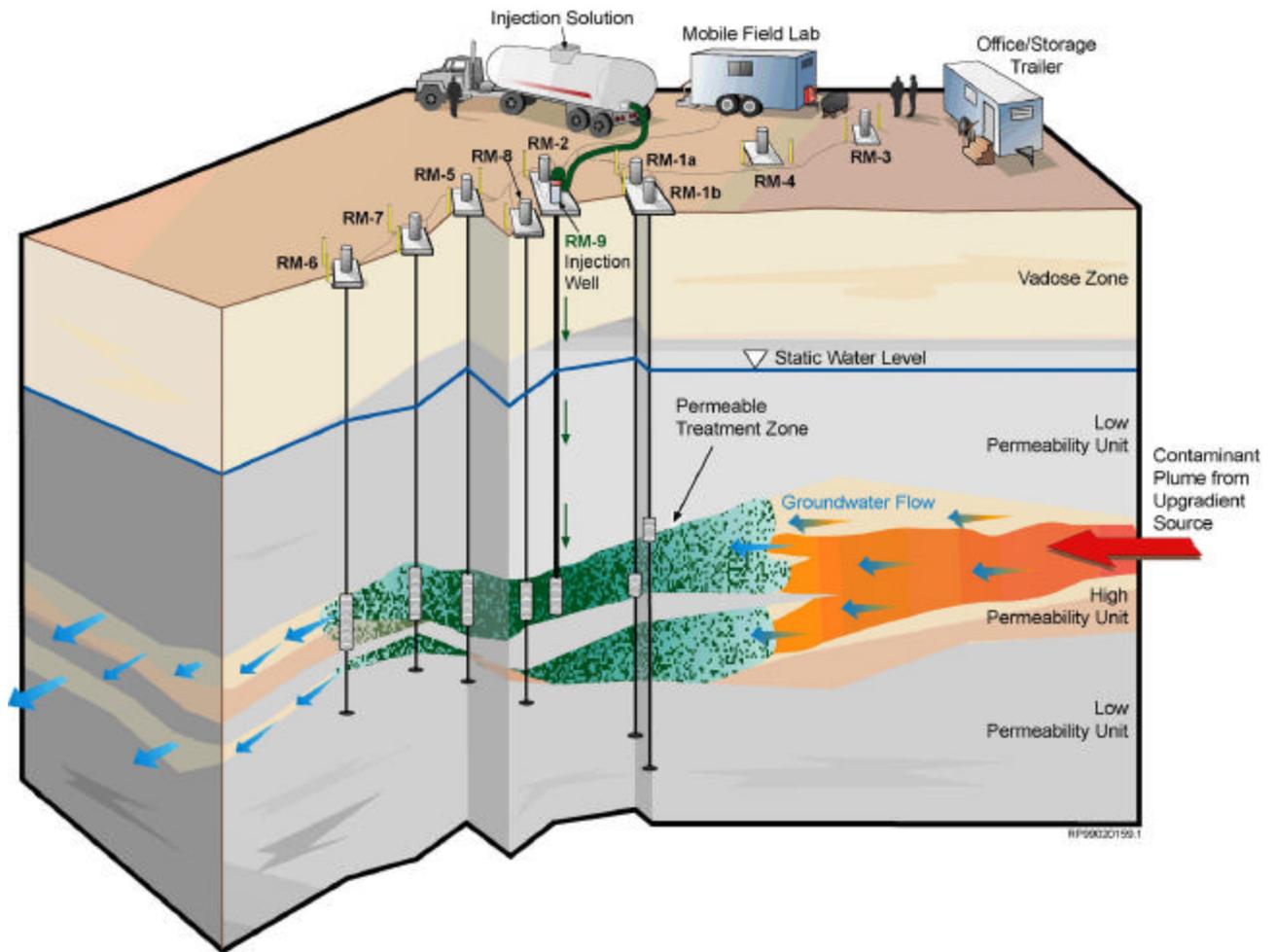


Figure 1.3. In Situ Redox Manipulation Conceptual Diagram. Schematic hydrology shown in diagram is based on the ISRM proof-of-principle test site at the Fort Lewis Logistics Center.

(Williams et al. 1999a), and a 2,000-foot-long ISRM barrier currently under construction at the same 100-D Area location. In addition, for each of these sites, batch and column tests were conducted to investigate the release of trace metals and gain regulatory approval for the field-scale injection. Results from these field- and laboratory-scale tests indicate that, although trace metals are mobilized (constituents of primary concern include iron, manganese, and arsenic) and exceed regulatory limits during the injection and withdrawal phases of the barrier emplacement, most are removed during the withdrawal, and following the emplacement do not migrate outside the reduced zone in significant enough quantities to create a regulatory concern. In addition to the mobilization of trace metals, poor recovery during the withdrawal phase of the treatment zone emplacement can result in a significant mass of reaction products (i.e., residual chemicals) remaining in the aquifer. The primary reaction product of the dithionite injection is sulfate, which is

regulated under a secondary drinking water standard. All constituents of concern were included in the operational and performance monitoring programs for the ISRM pilot test.

Analysis of hydraulic performance data from ISRM field demonstrations to date (Fruchter et al. 2000; Williams et al. 1999a) has not indicated a significant reduction in formation permeability from deployment of the ISRM technology. The hydraulic test analysis did indicate a near-well decrease in permeability at the injection/withdrawal well following the injection. This small zone of reduced permeability (i.e., skin effect) is attributed to entrapment of suspended or colloidal material, or mineralization associated with the carbonate buffer, in the sandpack zone and well screen during the withdrawal phase. This near-well reduction in permeability caused no adverse effects during the injection or withdrawal phases of the demonstrations and did not result in any significant degradation in the overall hydraulic performance of the treatment zone.

Another secondary effect associated with the ISRM technology that may be of concern at some sites is oxygen depletion. At the ISRM treatability test site at the Hanford 100-D Area, proximity to the Columbia River (~500 ft) and potential salmon-spawning habitat resulted in regulatory and stakeholder sensitivity. To address regulatory concerns, a modeling study simulated this near-river system and investigated mechanisms important to attenuation of the anoxic plume. The model predicted how far downgradient from the ISRM barrier acceptable dissolved oxygen concentrations were achieved (Williams et al. 1999b; Williams and Oostrom 2000). At the 100-D site, the numerical model predicted 75 to 95% oxygen saturation at the river and determined that air entrapment caused by water table fluctuations (associated with diurnal fluctuations in river stage) had the greatest impact on attenuation of the anoxic plume. Oxygen depletion is not expected to be a secondary effect of regulatory concern at FHC.

1.2 Field Test Objective

The objective of the In Situ Redox Manipulation Pilot Test was to determine the field-scale feasibility of this innovative remediation technology for the treatment of the hexavalent chromium contamination in the groundwater at the Frontier Hard Chrome site. Bench-scale studies using sediment from the FHC site have been conducted (Szecsody, 2002) with favorable results. However, a field test is required to determine the feasibility at a larger scale in the complex hydrogeologic and geochemical conditions of the subsurface. Data from the ISRM pilot test will be used to determine the feasibility of, and develop the remedial design for, a full-scale ISRM barrier at this location.

1.3 Report Organization

A discussion of the ISRM pilot test site characterization activities and conceptual model development is provided in Section 2. Site setup is summarized in Section 3. Details of the tracer test and treatment zone emplacement are contained in Sections 4 and 5, respectively. Section 6 assesses the preliminary performance of the emplaced treatment zone and conclusions are provided in Section 7. References cited

in the text are listed in Section 8 and supporting documentation, including well logs and as-built diagrams, electromagnetic borehole flow meter testing results, and tracer/dithionite breakthrough curves, can be found in the appendixes.

2.0 Pilot Test Site Characterization

This section contains a description of the well network installed at the pilot test site and a discussion of the geologic, geochemical, and hydrologic characterization activities conducted to refine the site specific hydrogeologic conceptual model. This more detailed conceptual model was used to guide the design process for emplacement of an ISRM treatment zone at the FHC pilot test site.

2.1 Well Installation

This section describes the field activities associated with installation and sampling of two injection wells and 11 monitoring wells at the FHC ISRM pilot test site (Figure 2.1). Information regarding the drilling method, nominal well diameter, screened interval, and radial distance from each injection well is provided in Table 2.1. As indicated in Table 2.1, three different drilling methods were used to install wells at the site, including sonic, hollow-stem auger, and direct push (GeoProbe) methods. This approach, although not ideal due to differences in sediment core sample quality and well installation/completion methodologies between the various drilling methods, was adopted in an attempt to provide sufficient monitoring wells to monitor the treatment zone emplacement while staying within the limited drilling budget.

Wells at the site were installed in two separate campaigns. During the initial drilling campaign (May 2002), designed to provide site-specific characterization information and the initial well network needed to monitor the ISRM injection tests, one injection well (INJ-1) and 11 monitoring wells were installed at the site. Based on results from the tracer injection test, it was determined that a second injection well (INJ-2) would be required. INJ-2 was installed by hollow-stem auger in August, 2002.

For the five monitoring wells installed using hollow-stem auger and the one installed using the sonic drill, a 6-in. borehole was advanced to total depth and completed with 2-in. PVC casing and screen. Screen material consisted of 10-slot continuous wire wrap (v-wire) screen and was set in a 20/40 Colorado silica sand filter pack. For the five monitoring wells installed using the direct push method, 3.25-in. drill rod was advanced to total depth and completed with 2-in. PVC casing and screen. Screen material consisted of slotted pipe (10-slot) with native formation as the filter pack (i.e., drill rods were back-pulled, allowing native formation to collapse around the screen). For the two injection wells installed at the site, one by the sonic method and the other by hollow-stem auger, a 10-in. borehole was advanced to total depth and completed with 6-in. PVC casing and screen. Screen material consisted of 20-slot continuous wire wrap (v-wire) screen and was set in a 10/20 Colorado silica sand filter pack. Table 2.1 contains well construction information for the 13 wells installed at the site, including drilling method, well diameter, screen interval depth, and radial distance from each injection well. Detailed well construction information is

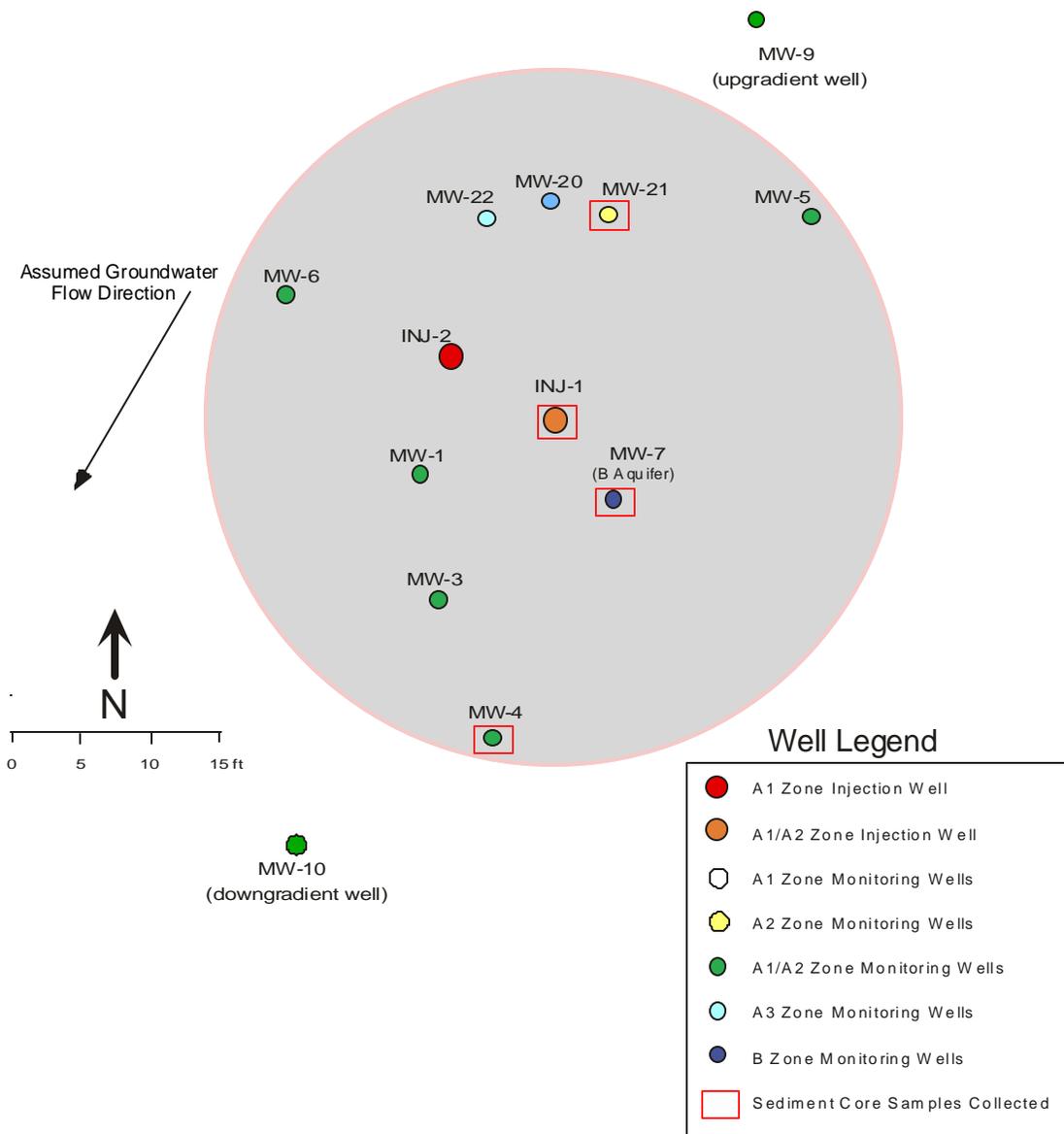


Figure 2.1. Well Layout at the ISRM Pilot Test Site

Table 2.1. Well Completion Summary Information

Well ID	Drilling Method	Casing Diameter	Depth Interval (ft bgs)	Radial distance from INJ-1 (ft)	~ Radial distance from INJ-2 (ft)
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INJ-1	Sonic	6-in	A zone: 20-35	--	8.8
INJ-2	Auger	6-in	A zone: 22-27	8.8	--
MW-1	Auger	2-in	A zone: 19.5-34.5	10.5	8.9
MW-20	Auger	2-in	A zone: 22-27	15.1	13.1
MW-21	Auger	2-in	A zone: 30-35	15.3	15.1
MW-22	Geoprobe	2-in	A zone: 35-40	15.1	10.2
MW-3	Auger	2-in	A zone: 22-37	15.4	17.7
MW-4	Auger	2-in	A zone: 20-35	23.1	27.6
MW-5	Geoprobe	2-in	A zone: 20-35	23.3	27.5
MW-6	Geoprobe	2-in	A zone: 20-35	21.3	12.5
MW-7	Sonic	2-in	B zone: 42-47	7.0	15.4
MW-9	Geoprobe	2-in	A zone: 20-35	31.9	32.2
MW-10	Geoprobe	2-in	A zone: 20-35	35.4	36.5

contained in the geologic logs and monitoring well installation reports contained in Appendix A. Installation and completion of these wells was conducted in accordance with Washington Administrative Code Standards (“Minimum Standards for Construction and Maintenance of Wells,” Chapter 173-160).

Samples were collected from four of the 13 boreholes (the two sonic boreholes and two of the hollow-stem auger boreholes, as indicated in Figure 2.1) for lithologic description, physical property analysis, and geochemical analysis (i.e., reducible iron content). Differences in sediment core sample quality was observed between the 4-in cores collected by the sonic method and the smaller diameter core (2.5-in) collected using the hollow-stem auger method. Comparison of particle size distribution data between the two sampling methods indicate that the smaller sampler was not appropriately sized for the gravel fraction at the site and thus skewed the particle size distributions toward the smaller size fraction. Due to the nature of the drilling methods used to install the remainder of the wells, limited additional lithologic information was obtained.

All site monitoring wells were developed prior to the initial baseline groundwater sampling event. Well development was conducted in two phases. The first phase consisted of limited bailing and/or surging, as required, during well completion (i.e., after placing the filter pack but before placing the annular seal) to settle the sandpack and remove fine-grained material generated during drilling. Immediately following well completion, an appropriately sized pump was installed, and the wells were pumped and surged until any remaining fine-grained material was removed from the installation and the well had achieved an acceptable yield and turbidity level. Several of the hollow-stem auger wells required additional development with a more aggressive surge block to achieve an acceptable yield. The injection well installed during the second drilling campaign using the hollow-stem auger method (INJ-2) showed a limited response to a similar development regime (i.e., aggressive surge blocking, jetting, and sand pumping). Due to the failure of these methods to achieve an acceptable well yield, an inflatable packer was installed and pressurized water injection was used to develop the screen interval. Although substantial well screen inefficiency (i.e., skin effect) still remained following this procedure, the yield of INJ-2 was improved enough to meet project requirements.

2.2 Hydrogeologic Characterization

Project constraints limited the number of locations where sediment core samples were collected for lithologic description and physical property analysis. As a result, precise contact depths for the various hydrostratigraphic units identified at the site were only available at a few select locations. Although

additional information would have improved the overall conceptual understanding of the site, sufficient information was collected to develop a generalized site specific hydrogeologic conceptual model (Figure 2.2). As indicated, the hydrogeology encountered beneath the ISRM pilot test site was much more heterogeneous than the original idealized hydrogeologic conceptual model of the site. The refined conceptual model consists of, in descending order, hydraulic or construction fill to a depth of ~ 10 ft, a clayey silt layer ~10 ft thick, a silty sandy gravel layer ~5 ft thick (referred to here as the A1 zone), another silty sandy gravel layer ~8 ft thick (referred to here as the A2 zone) that has an estimated hydraulic conductivity value an order of magnitude higher than that for the A1 zone, and a sandy gravel layer ~ 5 ft thick that was estimated to be approximately another order of magnitude higher in hydraulic conductivity (A3 zone).

Summary results from particle size distribution analysis of collected sediment core samples along with best estimates of other physical and hydraulic properties for each zone are shown in Figure 2.2. A detailed discussion of sediment physical property analyses and results are contained in Szecsody et al. 2002. It should be noted that the average hydraulic conductivity values were derived from analytical methods that, although valid for a layered system, are based on a homogeneous porous media concept and do not account for heterogeneities within each layer (see discussion in 2.4). As will be discussed in subsequent sections describing results from the electromagnetic borehole flow meter testing, tracer injection testing, and dithionite injection testing, evidence of formation heterogeneity was observed. However, the indicated values do provide a qualitative estimate of average hydraulic properties for the layered system. These characterization results in conjunction with vertical Cr(VI) profiling done by EPA prior to the pilot test, indicating that the highest concentrations of Cr(VI) measured at the site were within the A1 zone (Figure 2.4), demonstrated the importance of fully characterizing the hydrogeologic complexities present within the extent of the proposed treatment zone and the need to incorporate these complexities into the ISRM treatment zone emplacement design.

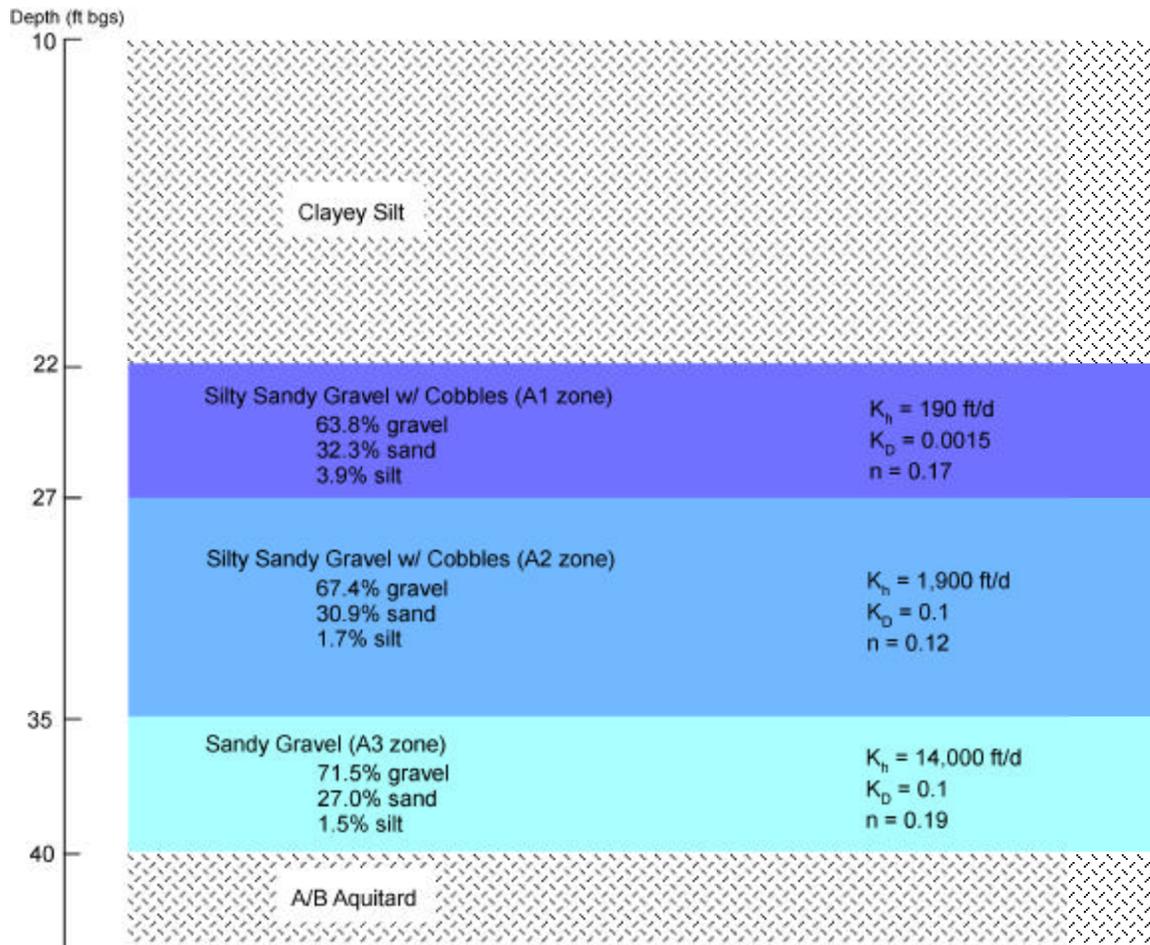


Figure 2.2. Generalized Hydrogeologic Conceptual Model of the ISRM Pilot Test Site

A similar cross-section showing the screened interval of all wells installed at the pilot test site is shown in Figure 2.3. Due to the requirement that all planned monitoring wells be installed in a single drilling campaign, most of the wells installed at the site were completed based on the original hydrogeologic conceptual model (i.e., no discernable layering within the A zone, Figure 1.2) and the Cr(VI) profile data collected by EPA (Figure 2.4). As indicated in Figure 2.3, the majority of monitoring wells intercept multiple aquifer units which limits their usefulness for interpreting tracer and reagent arrivals. It should be noted that interpretation of the ISRM treatment zone emplacement data was limited by this lack of suitable wells, i.e., wells capable of providing depth discrete data from each of the hydrostratigraphic units identified at the site.

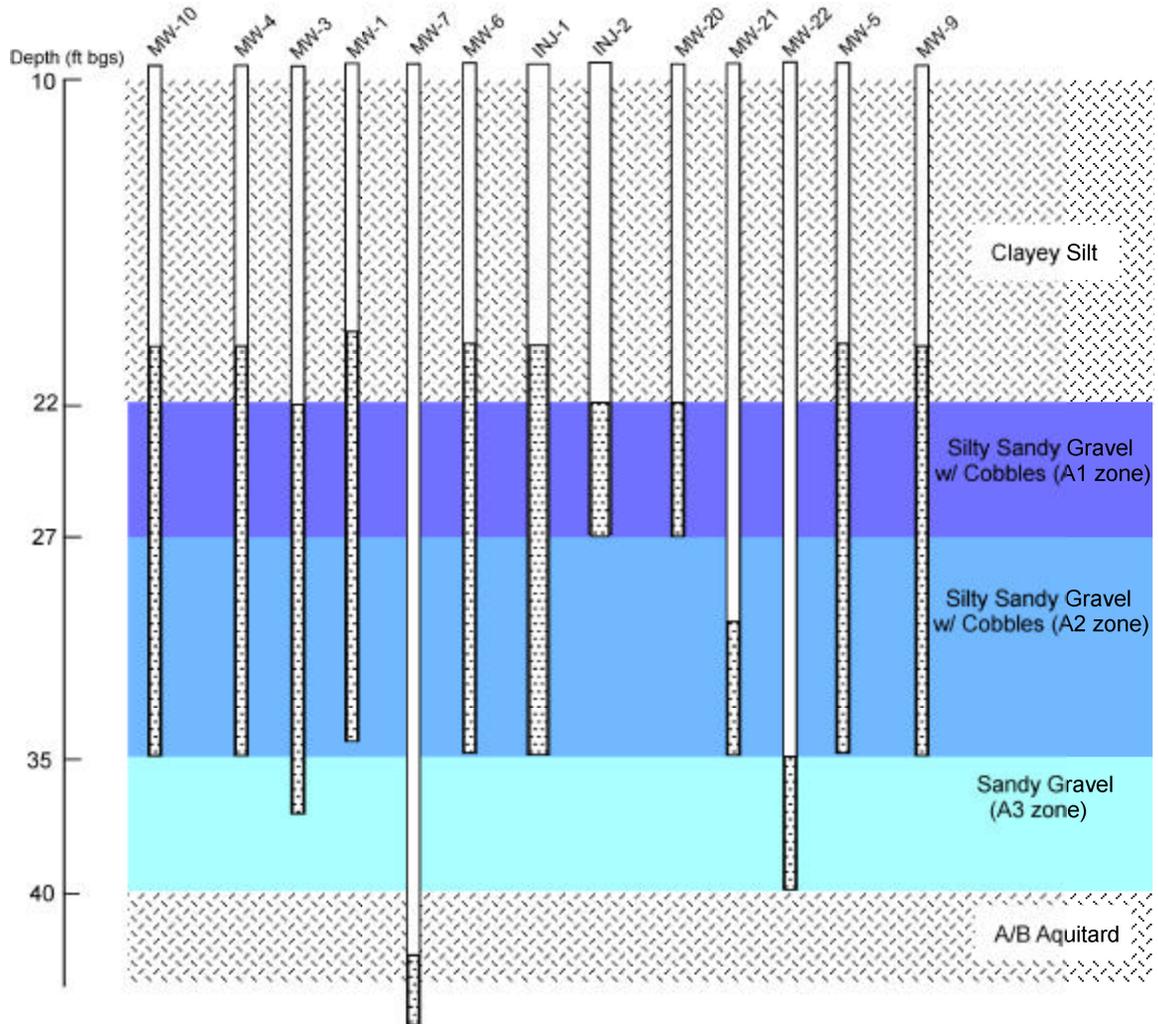


Figure 2.3 Monitoring Well Screened Intervals at the ISRM Pilot Test Site

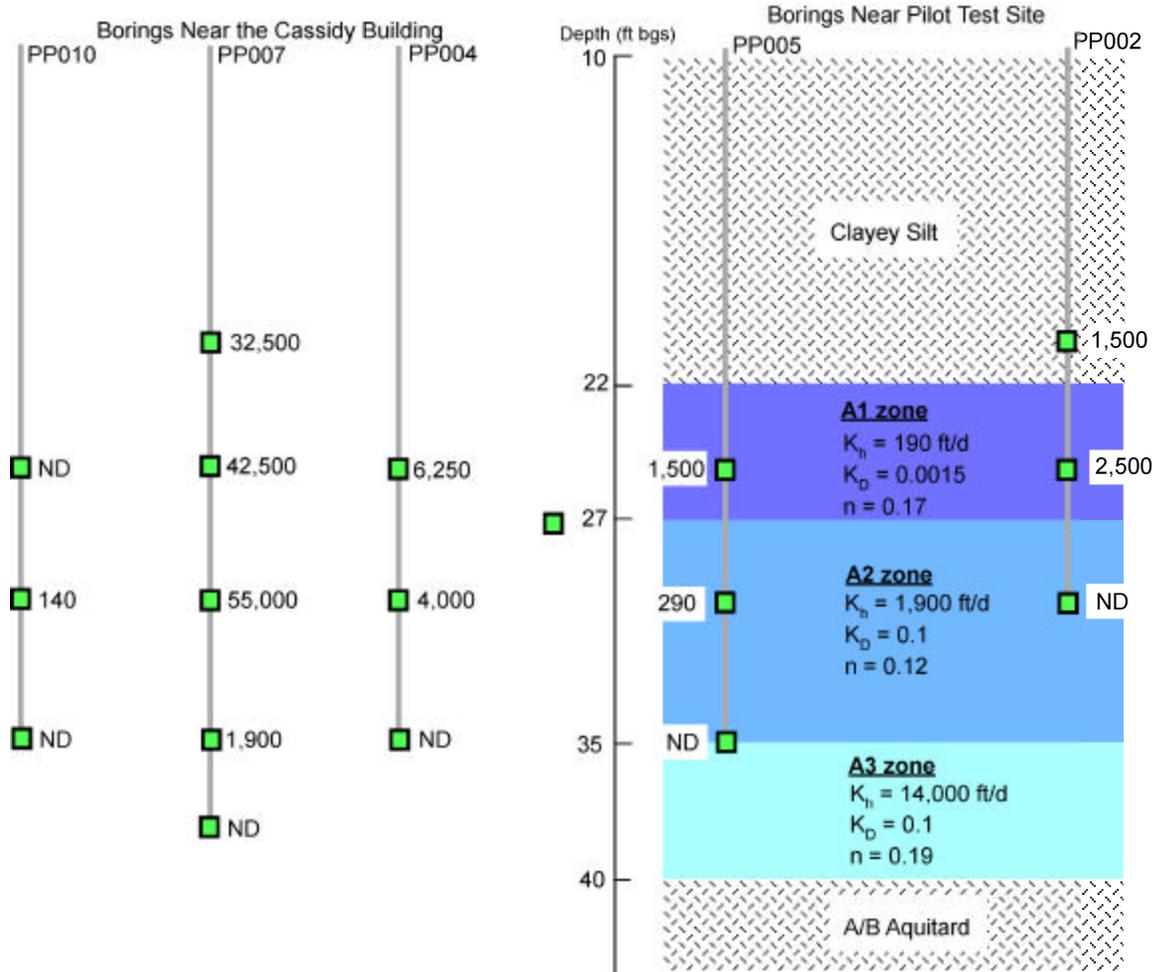


Figure 2.4. Aqueous Cr(VI) Concentrations (µg/L) Measured During Vertical Profile Sampling at the Site

2.3 Geochemical Characterization

Laboratory tests were conducted on 16 sediment core samples collected from four boreholes (across multiple depth intervals) to determine the reducible iron content, and spatial distribution of iron, for the targeted treatment zone. Laboratory experiments showed that chemical reduction yielded a redox capacity (0.26% Fe^{II}) that falls within the range of values observed in sediments analyzed from sites where field-scale deployment of the ISRM technology is currently in progress or being considered (0.1% Hanford WA 100D area, 0.24% Ft Lewis WA, 0.4% Moffett Federal Airfield CA, 0.3% in preliminary FHC samples). These analysis also indicated relatively low spatial variability in reducible iron content although some depth dependent variability was indicated. A detailed discussion of sediment geochemical analyses and results are contained in Szecsody et al. 2002.

The mass of reducible iron present in FHC sediments represents a sufficient quantity for an ISRM barrier to remain anoxic for 100s of pore volumes, which would be expected to last tens of years, depending on groundwater velocity and the concentration of oxidizing species in the groundwater. Although groundwater velocity and oxidizing species concentrations have not yet been well characterized at this site, the following example calculations, which are based on a 30 ft barrier width, an assumed groundwater velocity of 2 ft/d, and the measured reducible iron content in laboratory reduced sediments (i.e., fully reduced), provide a qualitative estimate of barrier longevity over the range of expected oxidizing species concentrations at the site. For the indicated barrier and flow conditions and inlet groundwater concentrations of 2.5 mg/L dissolved oxygen and 4 mg/L Cr(VI), the barrier would be expected to last for 75 years. For these same conditions with the Cr(VI) concentration increased to 55 mg/L, the barrier would be expected to last for 18 years. As indicated above, these sample calculations are for fully reduced sediments and thus represent the maximum possible reductive capacity. The actual barrier longevity will be effected by the efficiency of the field-scale emplacement processes and will be designed to meet remedial action objectives.

2.4 Hydrologic Characterization

This section describes analysis results from two short-duration constant-rate injection tests that were conducted at the ISRM pilot test site to provide the site specific hydraulic property estimates needed to develop a treatment zone emplacement design. Also discussed is a series of electromagnetic borehole flow meter tests that were conducted to characterize the vertical distribution of horizontal hydraulic conductivity and formation heterogeneities encountered at the site.

Hydraulic tests conducted at the site were limited (both in injection rate and duration) due to schedule, budget, and waste disposal constraints, and were designed to provide semi-quantitative estimate of areal hydraulic properties within the region affected by the targeted treatment zone. The first constant-rate injection test, conducted on June 13, 2002, was run at a constant rate of 50 gpm for a duration of approximately 6 hrs. The test was run by injecting clean water from a local fire hydrant into a centrally located injection well (INJ-1) and monitoring pressure response in all site monitoring wells. Pressure response data were monitored using pressure transducers (10 and 20 psi, 0.1% of full scale accuracy) and continuously recorded using a Campbell Scientific data logger.

As discussed in Section 2.1, the hydrogeology encountered beneath the ISRM pilot test site was inconsistent with the original hydrogeologic conceptual model of the site. Subsequently, the initial

constant-rate injection test conducted in INJ-1, which was screened across both the A1 and A2 aquifer zones (Figure 2.3), provided test conditions that were not well suited to obtaining hydraulic property estimates for the A1 zone and thus resulted in a large degree of error in that estimate. With additional information from the tracer injection test (Section 4), it was determined that well INJ-1 would not be an effective treatment zone emplacement well so a new injection well was drilled (INJ-2, Figure 2.3). To improve hydraulic property estimates prior to finalizing the design for the dithionite injection test, a second constant-rate injection test was conducted in INJ-2 using the same approach described above. The test was conducted on September 12, 2002 and was run at a constant rate of 20 gpm for a duration of approximately 90 minutes. Due to the relatively low permeability of this zone and the relatively shallow static depth to water (~ 20 ft), an inflatable packer was required to pack off the screened interval and prevent injection fluid from overflowing the casing.

The analytical approach used to interpret the test responses was based on the RADFLOW Pumping Test Simulator developed by G.S. Johnson and D.M. Cosgrove at the University of Idaho. RADFLOW utilizes a two-dimensional numerical model that operates in cylindrical coordinates and inherently assumes lateral or radial homogeneity. As discussed previously in section 2.2, evidence of formation heterogeneity was observed. Although this analysis approach is not rigorously correct, it does provide a suitable approach for providing a qualitative estimate of average hydraulic properties for the layered system. The model is designed for constant-rate test analysis in confined or unconfined layered systems with fully or partially penetrating stress and observation wells. The simulator is capable of estimating pressure response in any situation where porous media conditions are not violated (e.g., confined aquifers, leaky aquitards, unconfined aquifers with delayed yield, borehole storage, partial penetration, or any combination of these conditions).

Response data from both the INJ-1 and INJ-2 constant-rate injection tests were used together to develop hydraulic property estimates for the layered system beneath the ISRM pilot test site. In general, the test conditions and response data from the first injection test (INJ-1) were of higher quality than that obtained from the INJ-2 test. However, because INJ-1 was screened across both the A1 and A2 aquifer zones, which resulted in test conditions that were not well suited to obtaining hydraulic property estimates for the A1 zone, there was a large degree of uncertainty associated with the A1 estimate (i.e., a unique solution could not be obtained without independent data for the A1 aquifer zone). In an attempt to improve this estimate, a second shorter duration constant-rate injection test was conducted in INJ-2. Although test response data from the A1 zone (MW-20) during INJ-2 test were indicative of high permeability channel flow within a lower permeability matrix (Cinco, Samaniego and Dominguez 1978, Cinco and Samaniego 1981) and did not provide a quantitative estimate of hydraulic properties for the A1 zone, these data did put an upper bound on the hydraulic conductivity of this layer and significantly improved estimates based on the combined test analysis. It should be noted that no discernable test response was observed in the other two monitored zones (MW-21 and MW-22 monitoring the A2 and A3 zones, respectively) during this test. Using the response data from each of these tests, an iterative approach was used to obtain a solution that best approximated both sets of data. The resulting best estimates of hydraulic properties for the layered system are shown in Table 2.2 and test response data from the INJ-1 and INJ-2 constant-rate injection tests are shown in Figures 2.5 and 2.6, respectively.

Table 2.2 Hydraulic Property Estimates

Hydrostratigraphic Unit	Hydraulic Conductivity (K_h)	Anisotropy Ratio (K_D)
A1	190 ft/d	0.0015
A2	1,900 ft/d	0.1
A3	14,000 ft/d	0.1

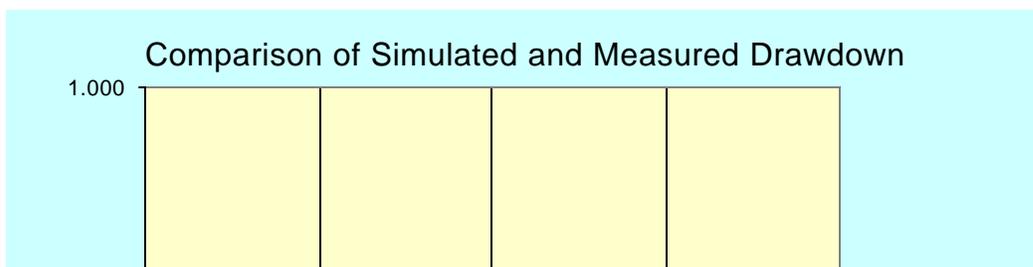
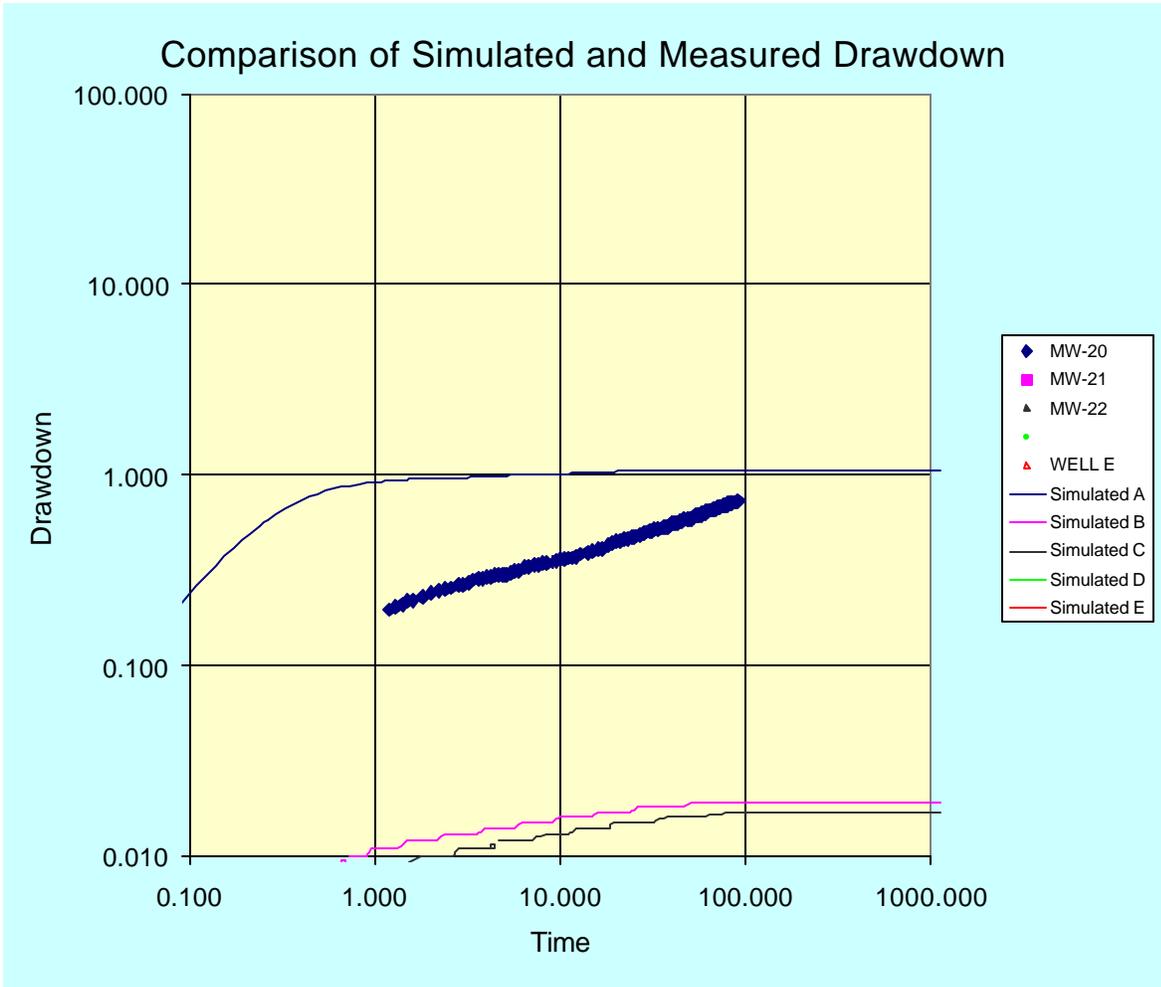


Figure 2.5 Test Response Data from the INJ-1 Constant-Rate Injection Test



To better characterize formation heterogeneities that were observed during the tracer injection test and provide additional information for design of the dithionite injection test, a series of electromagnetic borehole flow meter (EBF) tests were conducted in site monitoring wells. These data were useful in interpretation of tracer and reagent arrival curves and provided valuable guidance for placement of the alternate injection well (INJ-2) screen interval. Although a substantial volume of useful data was generated, a complete interpretation (e.g., spatial correlations between well location, geostatistical analysis, etc.) was not within the current project scope. If additional funding becomes available, a more rigorous analysis of the EBF testing results could provide additional insight into the scale of heterogeneities present at the site. A detailed discussion of the test methods and plots of the results are contained in Appendix B.

2.5 Baseline Groundwater Chemistry

Prior to initiation of any injection testing at the ISRM pilot test site, two rounds of groundwater samples were collected from all test site injection and monitoring wells (with the exception of INJ-2 which had not been installed yet). Samples were collected by EPA during the weeks of June 3 and June 10, 2002. Field parameters that were measured during the sampling events included electrical conductivity (EC), temperature, oxidation-reduction potential (ORP), pH, dissolved oxygen (DO), and hexavalent chromium. Laboratory analyses were also performed to measure common anions (ion chromatography, EPA-300.0) and trace metals (ICP-OES, EPA-SW-846 6010) concentrations.

Due to project constraints, data from the two baseline sampling events were not processed to the degree required for inclusion in this letter report (i.e., produce document quality tables, determine the data's statistical measures, etc.). Baseline Cr(VI) data, which is the most critical performance measure, are shown in Figure 2.7. These data, which represent the mean value for the two baseline sampling events, are also included in the discussion of ISRM treatment zone performance in Section 5.



Figure 2.7. Baseline Cr(VI) Concentrations at the ISRM Pilot Test Site

3.0 Pilot Test Site Setup

This section includes a description of the site utilities, monitoring equipment, analytical equipment, injection equipment, and the integration of these components into the operational systems required to conduct the tracer and ISRM injection tests at the FHC pilot test site. Weston will be responsible for providing all site utilities (with the exception of the boiler), PNNL will provide all required operational and monitoring equipment for the injection tests, and EPA will provide sampling/monitoring equipment for the baseline and performance assessment sampling and analytical laboratory services.

3.1 Site Utilities

Site utility requirements for this pilot-scale demonstration of the ISRM technology includes access to electrical power, water supply, and wastewater disposal.

To conduct the tracer and dithionite injection tests, a substantial source of water was needed to make up the injection solutions. At the ISRM pilot test site, a nearby fire hydrant supplied the water needed for dilution of the concentrated tracer and dithionite solutions; each test used over 40,000 gallons of water at rates as high as 50 gpm. For the tracer injection test, the concentrated tracer solution was mixed in an on-site ~4,500 gal polyethylene tank; the dithionite injection required no on-site storage tanks since the concentrated reagent was pumped directly from the tanker truck that delivered the chemical shipment.

Electrical power was required to operate site facilities, including a mobile laboratory and associated analytical equipment, process trailer, and injection/monitoring equipment. An appropriately sized electrical service panel was installed at the site which met all electrical requirements.

Wastewater was disposed of to the City of Vancouver's sanitary sewer system under special wastewater discharge authorization number 2002.11. The permit was obtained by EPA which gave authorization to discharge a certified non-hazardous "special wastewater" to the City of Vancouver's sanitary sewer system in compliance with the Pretreatment Program (Vancouver Municipal Code Chapter 14.10), and applicable provisions of Federal of State Regulations, and conditions contained in the discharge authorization. Specific conditions listed in the authorization included a range of permissible discharge dates, a maximum volume (60,000 gal), maximum rate (20 gpm), and several notification requirements. All pilot test wastewater was discharged to the sewer without incident.

3.2 Monitoring Equipment

Dedicated Grundfos RediFlo2 sampling pumps were installed in all site monitoring wells. The sample tubing from each of these sampling pumps was routed inside an onsite mobile laboratory and connected directly to a sampling manifold. Sample pumps were operated using a manufacturer-supplied variable-speed control box (converts standard 110-V single-phase power into three-phase power to meet the requirements of Rediflo2 sampling pumps) and a project-developed multi-channel interface (pump switch box) that allows multiple sample pumps to be operated using a single control box.

A project-developed sampling manifold was used to collect samples from the various monitoring wells. This approach routes all sample streams into a central manifold for monitoring field parameters (in a flow-through monitoring assembly) and collecting groundwater samples (Figure 3.1). The advantage of this type

of system is that all field parameter measurements are made using a single set of electrodes, which improves data quality and comparability of spatially distributed measurements. Consistent labeling between the sampling manifold and pump switch box simplifies selection of the well to be sampled and reduces the chance of operator error during the frequent sampling associated with the injection tests.

Field parameters were monitored using pH, ORP, temperature, electrical conductivity, and dissolved oxygen electrodes installed in a flow-through monitoring assembly. The flow-through assembly was designed to minimize the amount of “dead space” within the monitoring chamber and results in flow-through residence times of less than three seconds under standard monitoring conditions. Purge volumes pumped prior to sample collection were determined by monitoring stabilization of field parameters. The field parameter monitoring electrodes that were used during this field test meet the specifications shown in Table 3.1.

Table 3.1. Field Parameter Monitoring Electrode Specifications

Parameter	Manufacturer/Model #	Range	Accuracy/Reproducibility
pH	Oakton/WD-35615	pH 2–16	±0.05 pH
ORP	Metron/10-565-3116		
Temperature	Oakton/WD-35607	0.0–100°C	±0.5°C
Electrical conductivity	Oakton/WD-35607	0.0–199.9 mS	± 50 µS
Dissolved oxygen	Orion/810	0–20 ppm	± 0.1 ppm
Bromide (tracer test)	Cole-Parmer/P-27502-05	0.4–79,900 ppm	± 2% full scale

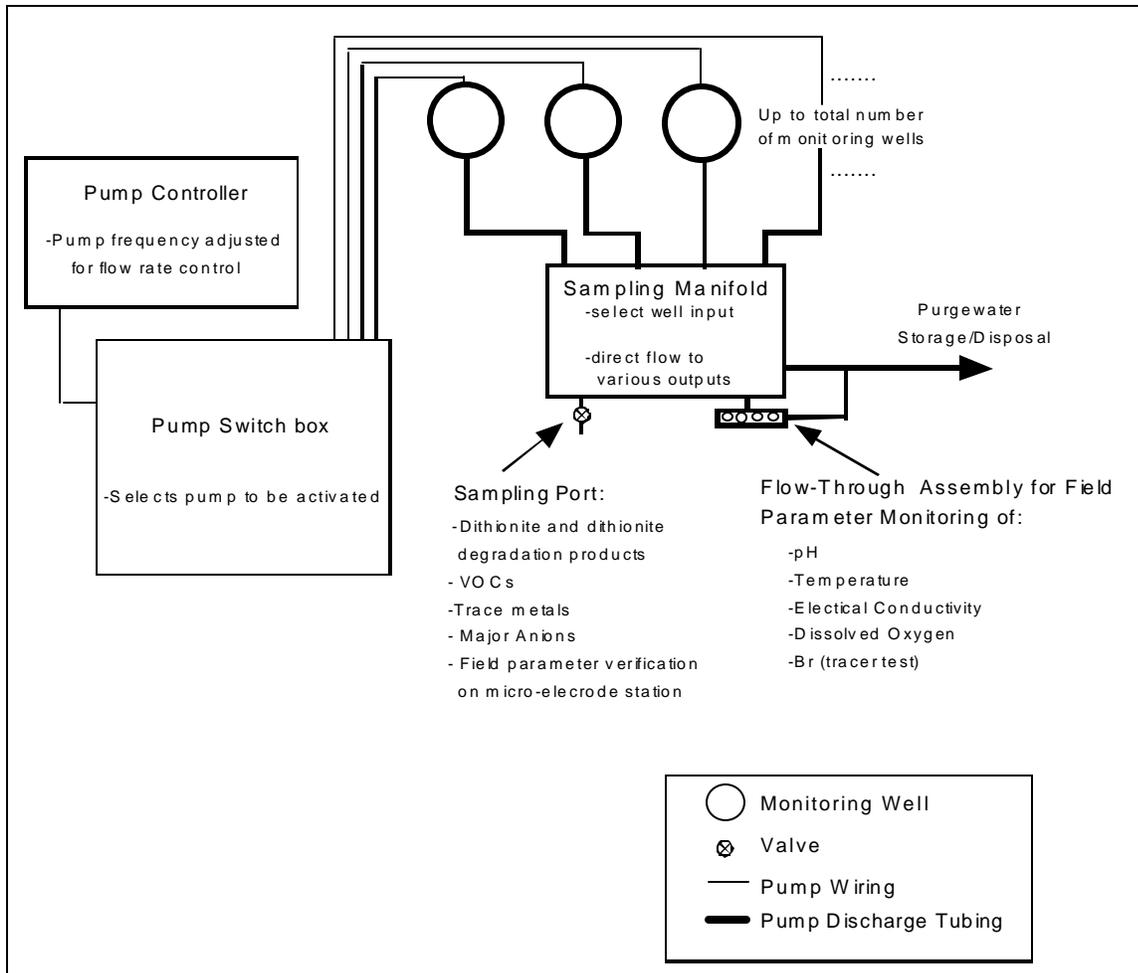


Figure 3.1. Schematic Drawing of the Groundwater Sample Acquisition System

Pressure transducers (10 and 20 psi, 0.1% of full scale accuracy) were installed in selected wells to monitor pressure response during hydraulic and dithionite/tracer injection tests and continuously recorded using a Campbell Scientific data logger. Water levels were measured using a high-accuracy, National Institute of Standards and Technology traceable, non-stretch, metal-taped, water level meter marked in 0.01 ft gradations.

3.3 Analytical Measurements

A comprehensive series of analytical measurements were made throughout the project in support of the field objectives. These included measurements made in Battelle's mobile laboratory during the injection/withdrawal tests, baseline and post-emplacement performance assessment monitoring performed in EPA's mobile laboratory, and samples submitted to EPA and contract analytical laboratories.

During the injection/withdrawal activities, dithionite measurements were performed in Battelle's laboratory using an ultraviolet absorption system with an on-line automatic dilution capability. Field measurement of dithionite were needed because of the inherent instability of that reagent, rendering analysis in an offsite

laboratory impractical. Dithionite calibration standards were freshly prepared in the field from pure reagent materials.

Trace metal samples were collected in 500-mL acid washed plastic bottles. Concentrated Ultrex nitric acid will included in each vial as a preservative. Baseline and performance assessment trace metals samples were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES; EPA 6010). Withdrawal samples were also analyzed for total sulfur ICP-OES. Ion chromatography was performed on unpreserved samples collected in 100-mL plastic bottles using EPA Method 300.0. In addition to these analytical measurements, samples were also analyzed on site for Cr(VI) using a spectrophotometric method.

3.4 Injection and Withdrawal Equipment

The injection manifold (Figure 3.2) consisted of an injection pump and appropriately routed piping, valving, and flow rate monitoring equipment. The manifold is used to control (both rate and concentration), monitor, and sample the injection solutions. The manifold was constructed of 316 stainless steel and used stainless steel ball valves for both diversion/shutoff and flow control valves.

A 0.75 hp Grundfos stainless steel multi-stage centrifugal pump (Model # CRN2-30) was used for injecting the concentrated solution. Due to the relatively low permeability of aquifer zone targeted (A1 zone) during the ISRM treatment in INJ-2 and the relatively shallow static depth to water (~ 20 ft), an inflatable packer (stainless steel with rubber bladder) was required to pack off the screened interval and prevent injection fluid from overflowing the casing. The injection tubing that extended from the well-head to the top of the inflatable packer was constructed of 1.5-in.-diameter stainless steel pipe. During the tracer injection test in INJ-1, this same 1.5-in.-diameter stainless steel pipe was used for the injection tubing which extended from the well-head to the center of the screened interval.

Omega® turbine flow meters were installed to measure the flow rate of the various streams and the total injection flow rate. Both 1-in and 2-in.diameter flow meters were available to provide for flexibility in the injection design. Appropriately sized flow meters were used to monitor the dilution water, concentrated tracer/dithionite solutions, and total injection rates. These flow meters were continually logged using a Campbell Scientific data logger.

An appropriately sized stainless steel submersible extraction pumps were used during the withdrawal phase of the tests. The extraction pumps were installed using either 1.5-in or 2-in.-diameter stainless steel riser pipe.

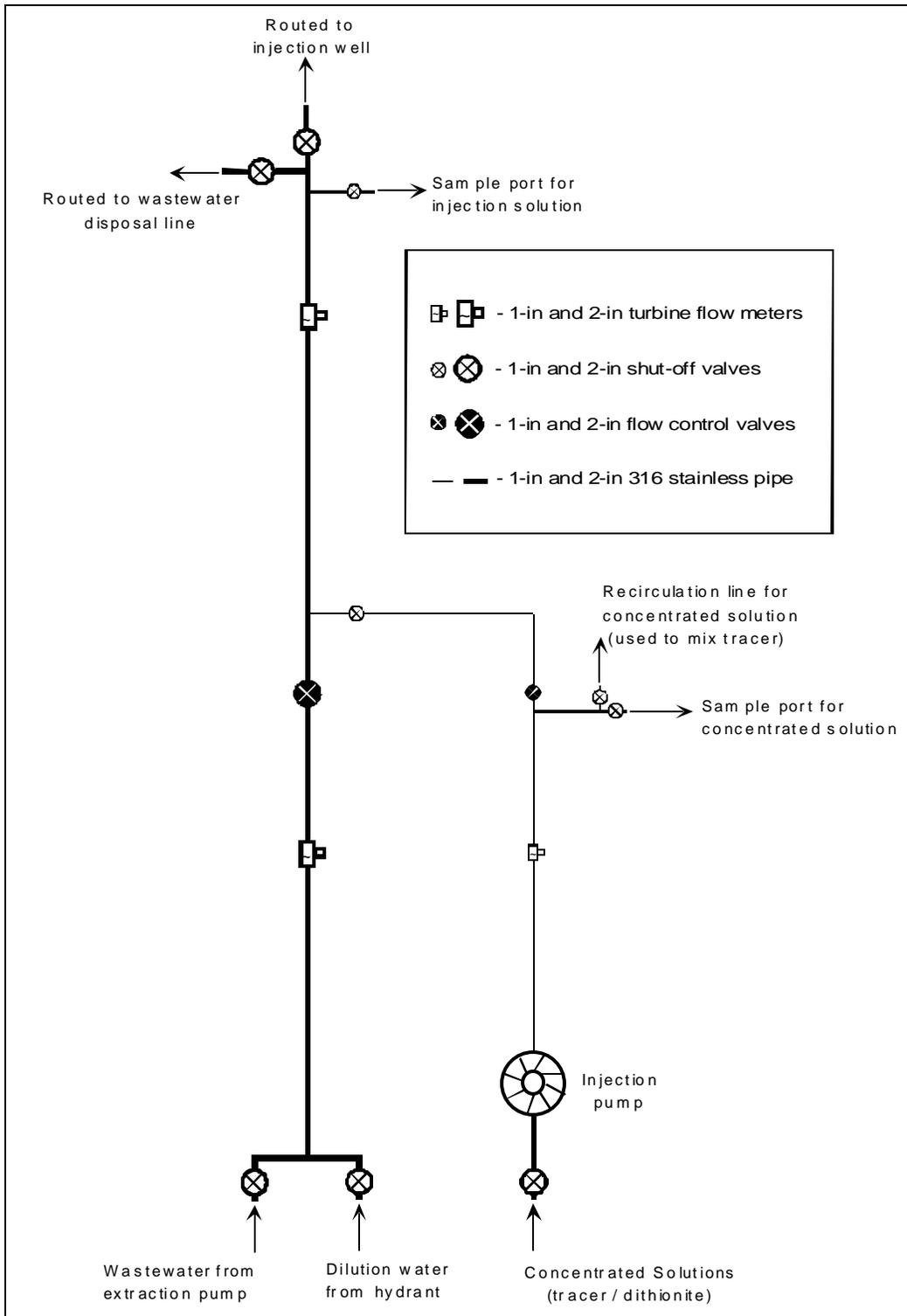


Figure 3.2. Schematic Drawing of the Tracer and Dithionite Injection System

3.5 Description of Equipment Integration/Operation

The tracer and dithionite injection tests were conducted using the equipment described above and illustrated in Figure 3.1. The desired injection concentration was achieved by mixing the concentrated tracer (tracer test) or dithionite (dithionite injection test) solutions with dilution water from the pressurized source. Injection pressure for the concentrated solutions and dilution water was provided by the stainless steel injection pump and the pressurized water supply (e.g., fire hydrant), respectively. The two injection streams were mixed within the injection manifold prior to reaching the point of injection (i.e., the center of the injection well's screen interval).

All injection flow rates (concentrated solution, dilution water, total) were monitored with turbine flow meters and controlled by manually adjusting flow control valves. Sample ports were located on the manifold so that samples of the concentrated and injection solutions could be collected throughout the injection test.

Following the injection and residence phases of the test, effort were made to remove remaining dithionite and reaction products through the central injection well using a submersible extraction pump. Wastewater generated during the withdrawal phase was routed back through the injection manifold to a wastewater disposal line that discharged to the sanitary sewer. Withdrawal water was routed back through the injection manifold so that the same flow monitoring and control equipment used to monitor/control the injection could be used to monitor/control the withdrawal.

Groundwater sample collection was conducted using the equipment described in Section 3.2 and illustrated in Figure 3.1. The groundwater sampling equipment consisted of dedicated variable-speed submersible sampling pumps installed in all site monitoring wells with sample tubing and control wiring routed to a central location inside the onsite mobile laboratory where groundwater field parameters were monitored (in a flow-through monitoring assembly) and groundwater samples were collected. The advantage of this type of system is that all field parameter measurements were made using a single set of electrodes, which improves data quality and comparability of spatially distributed measurements.

4.0 Bromide Tracer Test

4.1 Tracer Test Objective

A conservative tracer test was conducted at the ISRM pilot test site in June 2002 using a potassium bromide solution. The objectives of the tracer test, which were developed to aid in designing the dithionite injection test, included estimating the radial extent of injected solution, assessing spatial variability (heterogeneities) in the aquifer, testing field equipment, refining field operations, and determining sampling protocols. A description of the test and its results is provided below.

4.2 Tracer Test Description

The tracer test injected a solution containing a conservative, non-reactive tracer (Br^-) into a central injection well (INJ-1, as shown in Figure 2.1 and Figure 2.3). Bromide concentrations were measured in the injection stream and the surrounding monitoring wells to determine the arrival times and extent of the tracer plume. Table 4.1 summarizes the operational parameters of the tracer test. A concentrated potassium bromide (KBr) solution was prepared in a ~4,500-gallon tank and diluted in-line during the injection to the required concentration using the local water supply (fire hydrant). The volume of concentrated KBr solution prepared was 3,830 gallons with 16.9 kg of KBr. Injection rates were set at 5 gallons per minute (gpm) for the concentrated KBr solution and 45 gpm for the fire hydrant resulting in an injection concentration of 76 mg/L Br^- . The KBr solution was injected into the aquifer through the injection well (INJ-1) at 50 gpm for 12.8 hours, yielding a total injection volume of 38,600 gallons. Flow rates during the test were monitored using in-line turbine flow meters and recorded on a data logger (see Figure 4.1).

Aqueous samples were collected from the injection stream and from the surrounding monitoring wells to determine the extent of the tracer plume during the test. Bromide measurements for each well are provided in Appendix C. Bromide measurements for each well are also provided at two selected times, near the middle of the injection test and at the end, in Table 4.2. Bromide measurements were made during the test on samples collected in the mobile laboratory using ion-selective electrodes (ISE). Archive samples were also collected during the test and submitted to an off-site analytical laboratory for bromide measurements by Ion Chromatography (IC). During the tracer injection test, 184 aqueous samples were collected from the injection stream and surrounding monitoring wells and were analyzed in the field trailer for Br^- using three ion-selective electrodes. Two of the bromide electrodes were installed in the sampling manifold for in-line measurements. Another bromide electrode was used at a separate station for ISE bromide measurements from grab water samples with a stir plate and probe holder. Electrical conductivity (EC) and temperature were also measured using an in-line electrode in the sampling manifold. Three bromide electrodes were periodically calibrated during the test, using prepared calibration standards, over the range of temperature conditions encountered during the test. Of the 184 samples collected and measured during the test, 100 were selected for laboratory IC analysis. Bromide measurements shown in Appendix C used the IC analysis results for the 100 samples and the ISE measurements for the rest of the samples. The final calibration curves used for the ISE data shown in Appendix C were developed using the field ISE measurements and the laboratory IC bromide results. The breakthrough curves shown in Appendix C also include EC measurements since there was a significant difference in the EC between the injection bromide solution and the aquifer for some of the wells.

4.3 Tracer Test Results and Discussion

Bromide breakthrough curves (BTCs) were constructed for all of the monitoring wells during the test and are included in Appendix C. A summary of the concentrations midway through (~6 hrs) and at the end of the injection phase (~12 hrs) is provided in Table 4.2. At the time of the tracer test, Well INJ-2 was not installed. The BTCs and summary table show a significant variability in arrival times measured at the site that were not correlated with radial distance from the injection well.

Comparisons in tracer arrival behavior can be made using Wells MW-4, MW-5, and MW-6 since they have similar well completions (i.e., A1 and A2 screen intervals, see Figure 2.3) and are at similar radial distances from the injection well. Of these three wells, well MW-5 had the fastest tracer arrival with well MW-6 being the slowest. By the midpoint of the tracer injection, tracer concentrations in well MW-5 were twice as high as well MW-6 (see Table 4.2). Concentrations in well MW-4 were about 15% lower than MW-5 during the test. Overall, wells MW-4 and MW-5 had similar shaped tracer breakthrough curves, both with an initial rapid increase in tracer concentration during the first half of the injection followed by a slight increase (i.e., tail) during the second half of the test.

Another spatial comparison for similarly screened wells can be made with wells MW-1, MW-3, and MW-4 which are at increasing radial distances from the injection well toward the south. The completion for well MW-3 is slightly different than MW-1 and MW-4 since it penetrates the top of the A3 zone and is not screened in the upper clayey silt. The furthest of these three wells, MW-4, had the fastest tracer breakthrough with its tracer concentrations at the midpoint of the injection 1.3 times higher than MW-1 and 2.8 times higher than MW-3.

Two monitoring wells outside the targeted treatment zone at the greatest radial distance (> 30 ft) both had significant bromide concentrations during the tracer injection test. These are the upgradient and downgradient wells, MW-9 and MW-10, and are completed the same as the injection well INJ-1. Well MW-9, which is slightly closer to the injection well than MW-10, had faster arrival times and higher tracer concentrations than many of monitoring wells in the targeted treatment area (i.e. greater than MW-3 and MW-22, similar to MW-1 and MW-6). The downgradient well (MW-10) had a peak concentration of ~15% of the injection concentration.

Vertical variations in tracer arrival were also very significant as shown by tracer behavior in Wells MW-20, MW-21, and MW-22, which are similar radial distances from the injection well, but are screened in the A1, A2, and A3 zones, respectively. Arrivals in the lowermost zone (i.e. MW-22 in the A3) were the fastest even though the bottom of the injection well is screened above this unit. By the midpoint of the tracer injection, well MW-22 had tracer concentrations 2.9 times well MW-20 and 1.3 times well MW-21 as shown in Table 4.2. Similar concentration ratios were also measured at the end of the tracer injection test in these three wells. The breakthrough times and peak concentrations correspond to the relative hydraulic conductivity of the zones. As discussed in Section 2.4, zone A3 has the highest hydraulic conductivity and it had the fastest arrival time and largest peak concentration (i.e., well MW-22, see Appendix C and Table 4.2). Well MW-20 had the slowest arrival time and lowest peak concentration of this set of wells and is screened only in the A1 zone which had the lowest relative hydraulic conductivity. The relative tracer arrivals in these three wells can be explained by the proportionation of the total injection well flux between these three zones which is controlled by the relative hydraulic conductivity of these zones.

At the time of the tracer test, well MW-20 was the only well completed just in the A1 zone and it had very low tracer concentrations even though it was very close to the injection well. The maximum tracer concentration in this well was only ~1/3 of the injection concentration at the end of the test. Additionally, screening sampling of this well 12 hours following the tracer injection test showed that the tracer concentration dropped below 5% of the injection concentration and the hexavalent chromium concentration was similar to the very high pre-tracer test levels.

Well MW-7 was screened below the A Aquifer (below the A/B aquitard) to provide information on leakage through the aquitard from stresses applied in the injection well during the tracer test (See Figure 2.3). No

significant increases in bromide concentrations were evident in the ISE data or IC data. A slight decrease in EC was measured in this well during the injection test.

Overall, the tracer test showed that insufficient reagent would be injected into the A1 zone of the aquifer during ISRM treatment if the same injection well design was used for the dithionite injection test. Additionally, the tracer test showed that the site has a high degree of vertical and spatial heterogeneities. The A1 zone is the most important of the three A Aquifer zones for targeting ISRM treatment since the hexavalent chromium concentrations in this zone are much greater than the lower two zones. Results of the tracer test also showed that the A3 zone, which has relatively low hexavalent chromium concentrations, would receive the most reagent. The amount of reagent injected into the A1 using the original injection well (INJ-1) would be expected to be even less considering the increased density of the reagent used for ISRM treatment. Density effects of the reagent would also be expected to increase the amount of reagent in the lower A3 zone.

Based on the results of the tracer test, a new injection well was installed at the site (Well INJ-2) for use in the ISRM treatment zone emplacement (i.e., dithionite injection / withdrawal test). The new injection well is screened only in the A1 zone to limit the amount of reagent in the A2 and A3 zones which have much greater hydraulic conductivities. Given the uncertainties in the hydraulic conductivity, anisotropy, and importance of density effects on reagent sinking during dithionite injection, the injection design for the ISRM pilot test specified the use of the new injection well (INJ-2) only. Preliminary interpretation of the vertical spreading of the reagent plume during the tracer test indicates that it was not sufficient for treatment of the lower two A Aquifer zones and that a strategy of injection using two wells with different screen intervals (i.e., A1 and A2 separately) should be pursued to ensure the needed vertical barrier coverage of the A aquifer during full-scale deployment.

Another objective of the tracer test was to determine sampling protocols and test the field equipment. Testing of groundwater sampling protocols before and during the tracer test showed that a three-minute purge at 1 gpm (three gallons total) was sufficient prior to sample collection. This was based on the stability of measured parameters (ISE, temperature, pH, EC, and DO) when switching between wells. These resulting purge volumes are applicable only during forced gradient conditions at the site (i.e., during injection / withdrawal tests).

Table 4.1. Summary of Frontier Hard Chrome ISRM Site Dithionite Injection/Withdrawal Test

Test Parameter	Value
Tracer Mass	16.9 Kg (37.1 lbs) of Potassium Bromide (KBr)
Concentrated Tracer Solution Volume	3,830 gallons
Total Injection Rate	50 gallons per minute
Conc. Tracer Injection Rate	5 gallons per minute
Fire Hydrant Injection Rate	45 gallons per minute
Injection Concentration	76 mg/L Br-
Injection Duration	767 minutes (12.8 hrs)
Injection Volume	38,600 gallons

Table 4.2. Bromide Tracer Test Injection Concentration Summary

Well Name	Radial Distance Inj-1 (ft)	Mid-Injection Br ⁻ Conc. (mg/L)	Mid-Injection Br ⁻ %	End Injection Br ⁻ Conc. (mg/L)	End Injection Br ⁻ %
INJ-2	not installed	--	--	--	--
INJ-1	0.0	78	100	77	100
MW-1	10.5	42	54	62	81
MW-20	15.1	21	27	29	37
MW-21	15.3	46	59	64	84
MW-22	15.1	60	77	72	94
MW-3	15.4	20	25	28	37
MW-4	23.1	55	71	60	79
MW-5	23.3	64	81	68	89
MW-6	21.3	35	45	54	70
MW-7	7.0	0	0	0	0
MW-9	31.9	38	48	56	73
MW-10	35.4	3	3	11	14

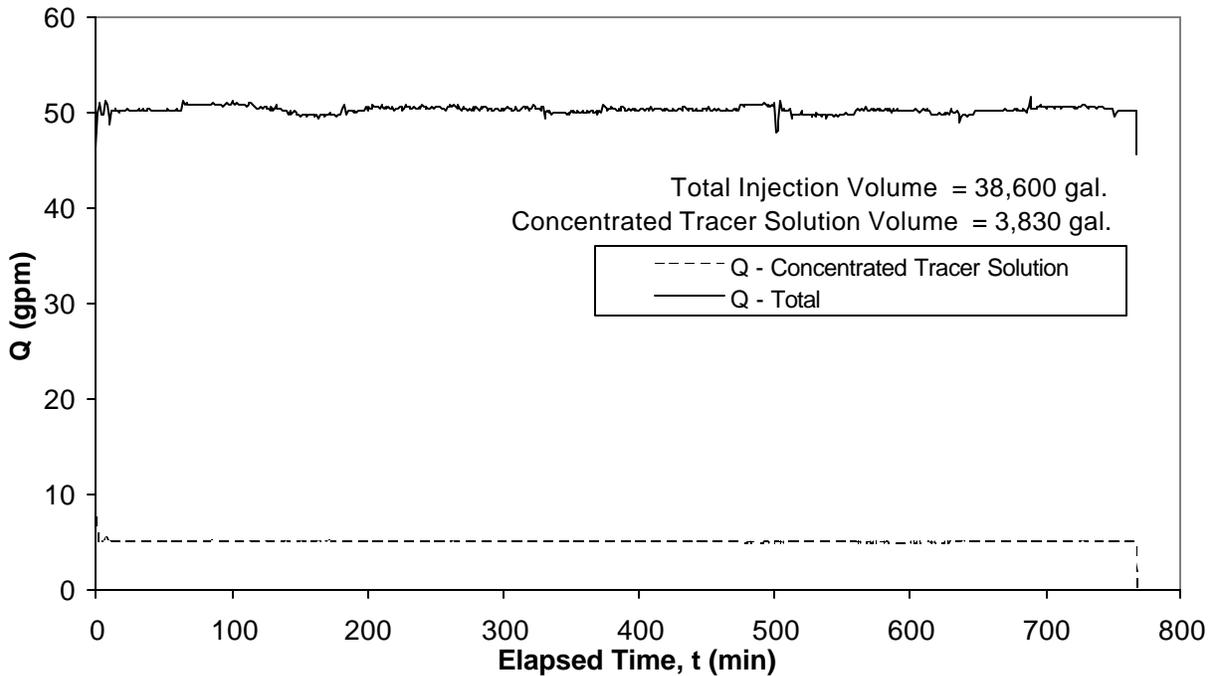


Figure 4.1. Frontier Hard Chrome ISRM Proof-of-Principle Site Bromide Tracer Test Showing the Rates, Duration, and Total Volumes Injected into the Injection Well (Well Inj-1)

5.0 ISRM Treatment Zone Emplacement

5.1 Emplacement Strategy

The ISRM treatment zone was created by injecting and withdrawing a sodium dithionite solution with a potassium carbonate pH buffer to reduce the naturally occurring Fe(III) in the aquifer sediments to Fe(II). During this test, which was conducted on October 17 through 20, 2002, reagent injection and withdrawal was performed in well INJ-2 (Figures 2.1 and 2.3) using an injection/withdrawal (or push-pull) approach that consisted of three phases: injection, residence, and withdrawal. In the injection phase, the solution is injected into a central injection/withdrawal well. The residence phase provides time for the reagent solution to react with the aquifer sediments and potentially drift in the aquifer. In the withdrawal phase, the solution is extracted from the aquifer by pumping from the same well used for injection. Well INJ-1 was also used in the withdrawal phase for extraction to help remove reaction products from the lower A Aquifer zones.

Bench-scale testing with aquifer sediments from the site (as detailed in the Bench-Scale Testing Letter Report, Szecsody et al., 2002) determined that these sediments contain a large amount of reducible Fe(III) (mean of 39 micrograms/mole). This amount of reducible iron is in excess of the reducing capacity of one tanker truck shipment of dithionite for the targeted treatment zone. If site sediments were fully reduced during the treatment, the reductive capacity of the aquifer, and therefore the barrier longevity, would likely be greater than needed to meet remediation objectives.

The objective of the dithionite injection/withdrawal tests was to create a reduced zone in the targeted portion of the aquifer (primarily unit A1, as shown in Figure 2.2) to significantly lower hexavalent chromium concentrations in groundwater migrating through the treatment zone. The objective of this pilot-scale test was also to gather information needed for the design of a full-scale ISRM barrier at the site. While the bench-scale studies had demonstrated the feasibility of the ISRM concept at a small scale, the field test incorporated all additional complexities of full-scale remediation (hydraulic conductivity and physical heterogeneities and their effect on reagent distribution, iron oxide spatial heterogeneity, etc.).

The injection/withdrawal well (INJ-2) and one monitoring well were screened in the A1 zone. As discussed in the previous sections, hexavalent chromium concentrations are the highest in the A1 zone and this zone has the lowest overall hydraulic conductivity of the three permeable zones comprising the A Aquifer. Based on the tracer test results, an injection well was needed to isolate the A1 zone in order to increase the amount of reagent injected to it. The vertical extent of the reagent plume below the A1 zone into the A2 and A3 were monitored during this test to see if adequate reagent coverage in these other zones was also achieved due to the flow field created by the injection into A1 and density effects from the reagent. An emplacement strategy using injection into two different screened intervals (A1 and A2 zones separately) would be required if the vertical reagent coverage was not adequate using only the A1 zone injection well. Most of the monitoring wells at the site are screened across the A1 zone, but also include the higher permeability A2 zone, and in one case both the A2 and A3 zones.

Operational parameters from the pilot ISRM dithionite injection test are summarized in Table 5.1. Flow rates for the test are shown in Figures 5.1 and 5.2 for the injection and withdrawal phases. Figure 5.3 provides the dithionite and EC measurements for the injection and withdrawal streams during the test. Dithionite and EC measurements for all the wells collected during the test are provided in Appendix D. These data are summarized in Tables 5.2 and 5.3 for the midpoint and at the end of the injection phase for all the wells at the site during the test. Appendix D also includes EC measurements for all the wells collected one day after the withdrawal phase was over. Analysis of the emplacement monitoring data and

performance of this test will help guide design for the full-scale barrier deployment at the site. A detailed description of the pilot ISRM dithionite injection test and a discussion of the results are provided below.

5.2 Emplacement Description

Approximately 5,700 gallons of concentrated sodium dithionite solution with a potassium carbonate pH buffer was delivered to the site in a tanker truck for the injection/withdrawal test. Prior to shipment to the ISRM site, the solution was chilled (during the dissolving process), and the headspace of the tank was blanketed with nitrogen gas to prevent oxidation with atmospheric oxygen. The molar concentration of potassium carbonate was four times that of the sodium dithionite to maintain a high pH for enhanced stability of dithionite. This results in a pH of 11 in the injection solution. The mass of chemicals used for the injection/withdrawal test is listed in Table 5.1.

The concentrated reagent was pumped directly from the tanker truck and diluted inline using a local water supply from a fire hydrant near the site. The volume of concentrated reagent in the tanker truck was calculated onsite from tank level measurements and was used to determine the injection rate of the concentrated reagent. The dithionite concentration was also measured from the tanker truck solution to verify the mass and purity delivered. A complete description of the process and analytical equipment used at the site is provided in Section 3. Dithionite was measured at the field site in a on-site mobile laboratory using two automated high-performance liquid chromatography (HPLC) systems connected to syringe pumps for sample dilution with anoxic water. Because of its instability, dithionite must be measured at the site shortly after sample collection. A blanket of argon gas was maintained within the tanker of concentrated dithionite solution throughout the injection to minimize reagent degradation from contact with atmospheric oxygen.

Injection into well INJ-2 began after the concentrated solution and dilution water flow rates had been determined and set. During all phases of these tests, aqueous samples were collected from the sampling manifold inside the field trailer. In-line probes were connected to the sampling manifold for direct measurement of temperature, EC, pH, DO, and Eh. Aqueous samples for dithionite measurement were collected directly into 10-mL syringes via a luer-lock fitting on the manifold to prevent oxidizing the samples with atmospheric oxygen. These samples were measured immediately after collection for dithionite concentration. Archive samples were also collected at the sampling manifold during the injection and withdrawal phase for laboratory analysis of sulfur, major anions, and trace metals. The samples collected for trace metals were filtered using a disposable 0.45 μm filter and preserved with ultra-pure nitric acid. Chemical data collected during the test were recorded on datasheets, entered into electronic spreadsheets, and plotted to monitor the progress of the tests.

Following the injection phase, the residence phase provided additional time for the dithionite to react with the aquifer sediments. Aqueous samples were collected during the residence phase and measured for dithionite and field parameters. The duration of the residence phase was determined by the estimated field-scale dithionite reaction and degradation rates and from dithionite concentrations measured at the site.

During the withdrawal phase, unreacted reagent and reaction products were extracted by pumping from the A1 zone injection/withdrawal well (INJ-2) and from the original injection/withdrawal well (INJ-1). The withdrawal water was disposed of to the City of Vancouver's sanitary sewer located southeast of the test site. Samples collected from the injection and withdrawal streams were analyzed for total sulfur, which accounts for the dithionite reaction products (sulfate, sulfite, and thiosulfate), and total dissolved solids (TDS). These data can be used to calculate a mass balance for the injection/withdrawal test (i.e., percent of injected reagent recovered). The total volume of water withdrawn during the withdrawal phase was approximately one injection volumes. The percentage of sulfur mass recovery was estimated for the

dithionite injection/withdrawal test (see Table 5.1) based on EC measurements of the withdrawal stream using a relationship between EC and total sulfur developed at other ISRM sites. This estimate will be updated using sulfur analysis data once it becomes available. The following sections provide additional details and discussion of the three phases of the test.

5.2.1 Injection Phase

The average reagent concentration for the pilot dithionite injection test was 0.1 M sodium dithionite with a 0.4 M potassium carbonate pH buffer. A total volume of 44,000 gallons of reagent was injected into well INJ-2 at a rate of 40 gpm for 18.3 hours. Aqueous samples were collected at roughly five-minute intervals with samples collected from the injection stream and all the monitoring wells every 1.25 hours on average. Breakthrough curves (BTCs) for dithionite and EC are provided for the injection/withdrawal well and the monitoring wells in Appendix D and summarized in Tables 5.2 and 5.3 at two times during the injection phase. Figure 5.3 shows the dithionite and EC measurements for the injection and withdrawal streams during the test.

Most monitoring wells did not indicate high dithionite and EC concentrations during the injection phase as shown in Appendix D and Tables 5.2 and 5.3. This was not unexpected since the injection was focused on the A1 zone and only one monitoring well (MW-20) is discretely screened in this lower permeability zone. The one exception to this was well MW-6 which had a very rapid arrival early in the injection phase. This well had an incomplete BTC due to a pump failure part way through the injection test.

While well MW-20 is completed only in the A1 zone and is relatively close to the injection well (INJ-2), peak EC and dithionite concentrations were less than 50% of the injection value in this well. Compared to the bromide tracer test (see section 4), this relative peak value was only slightly better than measured in the tracer test which used an injection well screened in both the A1 and A2 zones. Although the relative peak values were similar in these two tests for well MW-20, the character of the breakthrough curves differed with the EC rapidly increasing and then remaining level for the remainder of the injection phase during the dithionite test. Increasing concentrations were much slower during the tracer test in well MW-20 and occurred through most of the tracer injection. The rapid increase and plateau of concentrations in well MW-20 during the dithionite injection phase may represent a portion of the A1 zone at this location which is isolated from the injection well via low permeability zone. Heterogeneities within the A1 zone may be greater than in the lower two zones of the A Aquifer, but this is difficult to assess given the limited number of wells.

EC and dithionite measurements in the wells discretely screened in the A2 and A3 zones during the injection phase were very low (1% and less of injection dithionite concentrations). Data from these wells show that there was not much vertical spreading of the plume in these locations during the injection phase. The results of monitoring of the well screened below the A Aquifer, MW-7, showed no significant change in EC from the dithionite injection in the A1 aquifer during the test.

The wells screened across multiple A zones (including the A1 zone) that had significant (> 20%) breakthrough include wells INJ-1, MW-1, MW-3, and MW-6. Wells MW-3 and MW-6 had a larger relative breakthrough during the dithionite injection/withdrawal test than the bromide tracer test. Well MW-1 had a smaller relative breakthrough in the dithionite injection/withdrawal test than the bromide tracer test.

5.2.2 Residence Phase

The duration of the residence phase for the pilot dithionite injection test was 31.5 hours. Sampling frequencies for the wells during this phase of the test started at 2-hr intervals and was decreased to a 4-hr

frequency by the end of this phase. Very low levels of dithionite (< 0.2% of the injection concentration) were measured in site monitoring wells at the end of the residence phase. This decrease in dithionite concentrations was due to reaction with ferric iron, disproportionation, and density effects.

EC measurements in the wells with significant reagent concentrations during the injection phase (i.e., > 20% of the injection concentration) decreased dramatically during the residence phase. The most pronounced effect can be seen during the residence phase in Wells INJ-2 and INJ-1 (see Appendix D). EC measurements during the residence phase decreased by 77% for well INJ-2 and 72% for well INJ-1. The other wells with significant EC breakthrough during the injection phase had a greater than 50% decrease in EC measurements by the end of the residence phase (MW-1, MW-20, MW3). While an increase in concentration would be expected in wells screened in the lower portion of the A Aquifer if density sinking were the primary cause of this observed concentration decrease, the one well screened only in the A3 zone (MW-22) did not show this trend.

Dithionite concentrations also decreased substantially during the residence phase. While some of this decrease was due to density effects, reaction and disproportionation was also occurring which results in an increasing separation between the EC and Dithionite BTCs during the residence phase. This effect can be seen in all the wells listed above that had significant EC breakthrough during the injection phase.

5.2.3 Withdrawal Phase

During the withdrawal phase, 44,400 gallons were pumped from wells INJ-2 and INJ-1; this was approximately the same as the injection volume. Extraction rates and volumes are shown in Figure 5.2. EC and dithionite concentrations in the withdrawal stream and the individual wells are shown in Figures 5.3 and Appendix D. The majority of the withdrawal water was pumped from well INJ-1 at 15 to 20 gpm for 36.9 hr for a total extraction volume of 36,200 gallons. A total volume of approximately 8,200 gallons was extracted from well INJ-2 at a rate of ~5 gpm for 27.7 hours. Extraction from well INJ-2 was limited due to the lower hydraulic conductivity materials comprising the A1 zone and its ability to sustain a higher yield. Extraction from well INJ-2 was stopped early in the withdrawal phase due to a pump failure.

The sampling frequency of the withdrawal stream was high (~1/2 hr) at the beginning of the withdrawal phase and then it was decreased gradually to a 4-hr interval during the second half of this phase. Dithionite concentrations were very low in the withdrawal stream. Measurements quickly dropped below detection limits within a few hours of the start of the withdrawal. Overall withdrawal concentrations (reaction products) were very low relative to the injection concentrations based on EC data. Peak concentrations in the withdrawal phase were less than 20% of the injection concentration in the beginning of the phase and rapidly dropped to below 10% in the first few hours. Concentrations in INJ-2 slightly rebounded once extraction from that well was stopped as shown in Figure 5.3.

Aqueous samples from the withdrawal stream were collected for estimates of the mass recovery from the withdrawal phase (total sulfur and TDS) and for trace metals (ICP-OES) to obtain water quality parameters for determining suitable disposal. The results of these analyses were not available in time for inclusion in this report. An estimate of the recovery was calculated based on EC measurements from the withdrawal stream and previous relationships between EC and total sulfur developed at other ISRM sites. Given this approach, an estimated 5% of the total injection sulfur was recovered during the withdrawal phase. This estimate will be updated once the laboratory data are available.

5.3 Emplacement Results and Discussion

The results of the pilot dithionite injection test indicated that two injection wells, one targeting the A1 zone and the other targeting the A2 zone, will be required to adequately treat the entire

A aquifer zone. Based on the vertical spreading measured between the A2 and A3 aquifer zones during the bromide tracer test, the injection targeting the A2 zone should be able to treat both the A2 and A3 zones. In addition to improved reagent coverage, this design change should also result in improved residuals recovery over that observed during the pilot test. The pilot test injection was conducted using only the INJ-2 injection well (A1 zone) for emplacement of the treatment zone. The three depth discrete monitoring wells available at the site (MW-20, MW-21, and MW-22) indicated that, under these injection conditions, formation properties in the A1 zone prevented sufficient reagent from contacting the A2 and A3 aquifer zone sediments. These conditions resulted in most of the reagent remaining within the A1 zone where, due to the hydrogeologic and hydraulic properties of this zone, it was difficult to remove during the withdrawal phase. The design of reductive capacity needed in each of the three A Aquifer zones is dependent on the barrier longevity required, the concentrations of oxidizing species in these zones (i.e., dissolved oxygen and hexavalent chromium), and the groundwater flux in each of these zones.

Results from the pilot dithionite injection test, in conjunction with results from the tracer injection test, showed that the site has a very high degree of variability in hydraulic properties controlling the direction and extent of reagent transport and treatment capacity distribution during the emplacement process. This type of spatial variability likely will limit the potential injection well spacing because a conservative approach will be required that provides the highest likelihood of constructing a continuous barrier (i.e., minimizes the potential for holes in the barrier). Treatment of the A1 zone is the primary objective at this site given the much greater hexavalent chromium concentrations in this zone relative to the lower two A Aquifer zones. Pilot-scale testing activities have demonstrated the need for detailed characterization of hydrogeologic conditions and contaminant distribution along the length of the barrier. This information will be required to determine how much conditions change across the proposed barrier length relative to the pilot test site and how this will affect injection designs for full-scale deployment.

Table 5.1. Summary of Frontier Hard Chrome ISRM Site Dithionite Injection/Withdrawal Test

Test Parameter	Value
Injection Phase	
Reagent Mass	5,300 lbs 90% purity Sodium Dithionite (Na ₂ S ₂ O ₄) 15,000 lbs Potassium Carbonate (K ₂ CO ₃)
Tanker Truck Volume	5,736 gallons
Total Injection Rate	40.3 gallons per minute
Tanker Truck Injection Rate	5.2 gallons per minute
Fire Hydrant Injection Rate	34.9 gallons per minute
Injection Concentration	0.1 moles / L Na ₂ S ₂ O ₄
Injection Duration	1097 minutes (18.3 hrs)
Injection Volume	44,000 gallons
Residence Phase	
Duration	1,893 minutes (31.5 hrs)
Withdrawal Phase	
Total Withdrawal Volume	44,400 gallons
Total Withdrawal Mass	4.8 % of Injection Sulfur (based on EC / Sulfur trend analysis)
INJ-1 – Withdrawal Rate	15 - 20 gallons per minute
INJ-1 – Volume	36,200 gallons
INJ-1 – Duration	2,215 minutes (36.9 hrs)
INJ-2 – Withdrawal Rate	~5 gallons per minute
INJ-2 – Volume	~8,200 gallons
INJ-2 – Duration	1,662 minutes (27.7 hrs)

Table 5.2. Dithionite Injection / Withdrawal Test EC Concentration Summary

Well Name	Radial Distance Inj-2 (ft)	Mid-Injection EC (mS/cm)	Mid-Injection EC %	End Injection EC (mS/cm)	End Injection EC %
INJ-2	0	60.0	100	58.9	100
INJ-1	8.8	32.7	55	36.3	62
MW-1	8.9	27.0	45	35.4	60
MW-20	13.1	28.7	48	27.7	47
MW-21	15.1	0.5	1	1.7	3
MW-22	10.2	2.7	5	3.8	6
MW-3	17.7	28.4	47	30.1	51
MW-4	27.6	4.8	8	7.2	12
MW-5	27.5	7.0	12	11.3	19
MW-6*	12.5	48.0	80	48.0	81
MW-7	15.4	0.3	0	0.3	0
MW-9	32.2	0.8	1	1.7	3
MW-10	36.5	5.7	10	7.0	12

* MW-6 pump failed - using last sample value

Table 5.3. Dithionite Injection / Withdrawal Test Dithionite Concentration Summary

Well Name	Radial Distance Inj-2 (ft)	Mid-Injection Dithionite (moles/L)	Mid-Injection Dithionite %	End Injection Dithionite (moles/L)	End Injection Dithionite %
INJ-2	0	0.103	100	0.099	100
INJ-1	8.8	0.045	43	0.049	49
MW-1	8.9	0.027	26	0.039	39
MW-20	13.1	0.039	38	0.040	40
MW-21	15.1	0.000	0	0.000	0
MW-22	10.2	0.001	1	0.001	1
MW-3	17.7	0.032	31	0.034	35
MW-4	27.6	0.001	1	0.002	2
MW-5	27.5	0.004	4	0.011	11
MW-6*	12.5	0.077	75	0.077	77
MW-7	15.4	0.000	0	0.000	0
MW-9	32.2	0.000	0	0.000	0
MW-10	36.5	0.000	0	0.001	1

* MW-6 pump failed - using last sample value

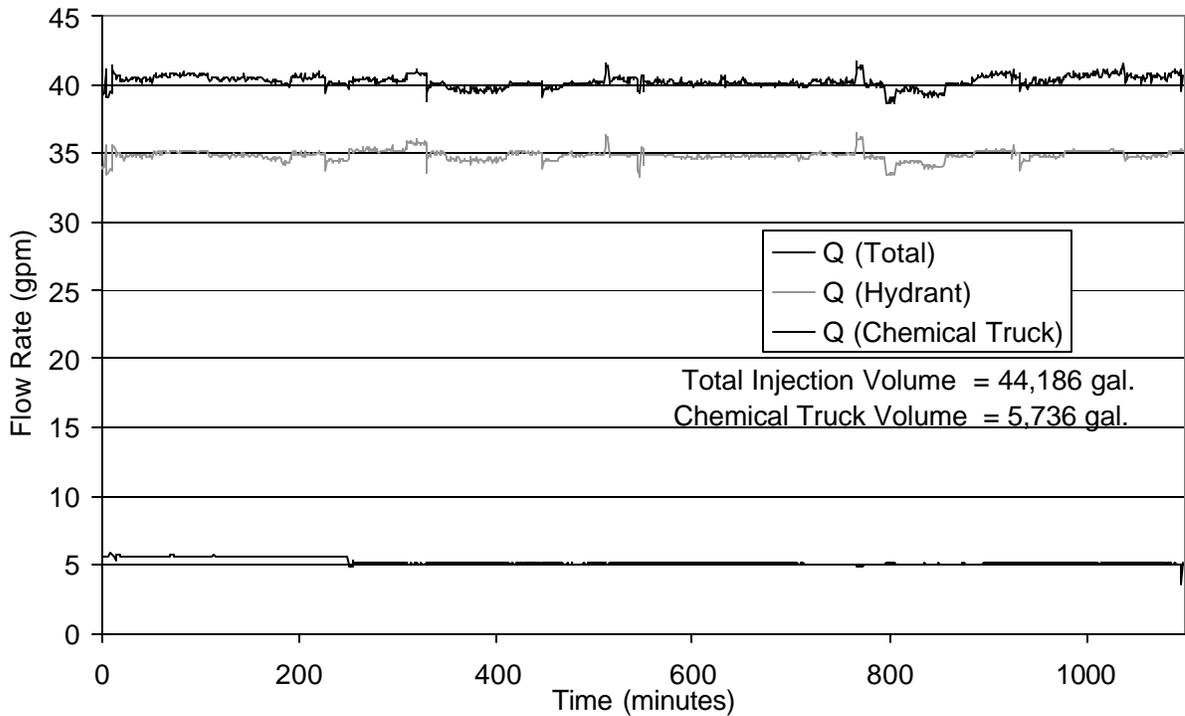


Figure 5.1. Flow Rates During the Injection Phase of the FHC Pilot-Scale Dithionite Injection/Withdrawal Test.

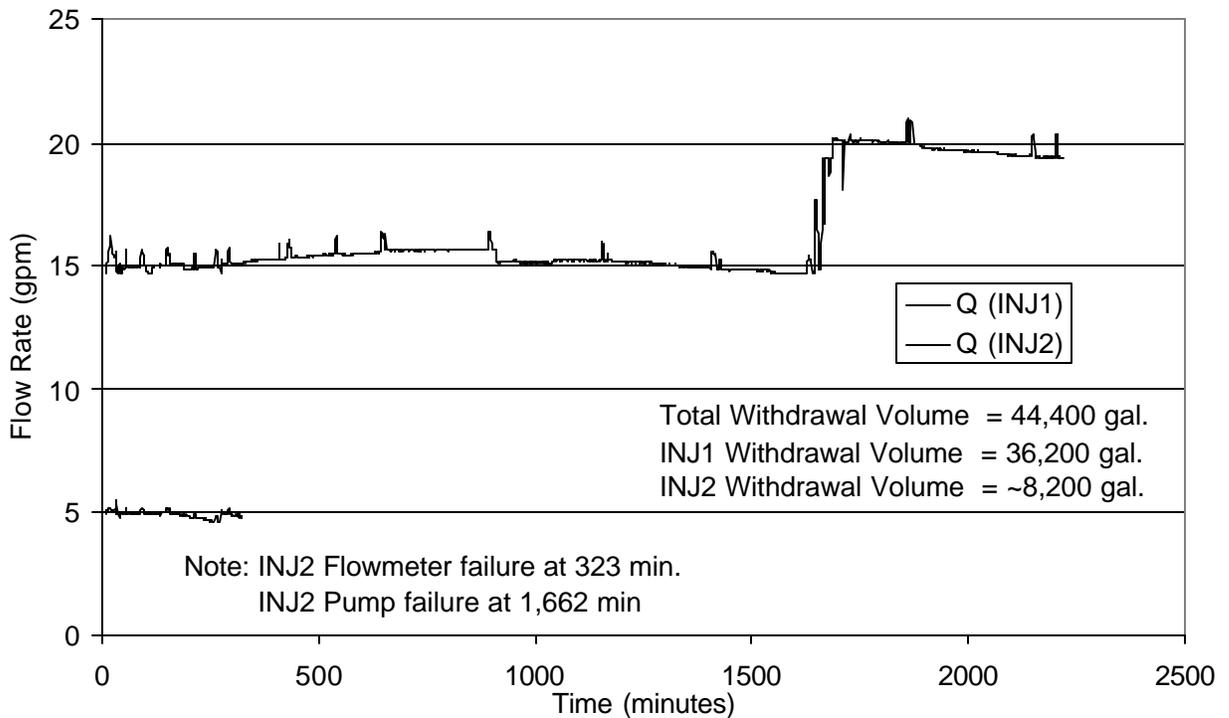


Figure 5.2. Flow Rates during the Withdrawal Phase of the Dithionite Injection/Withdrawal Test.

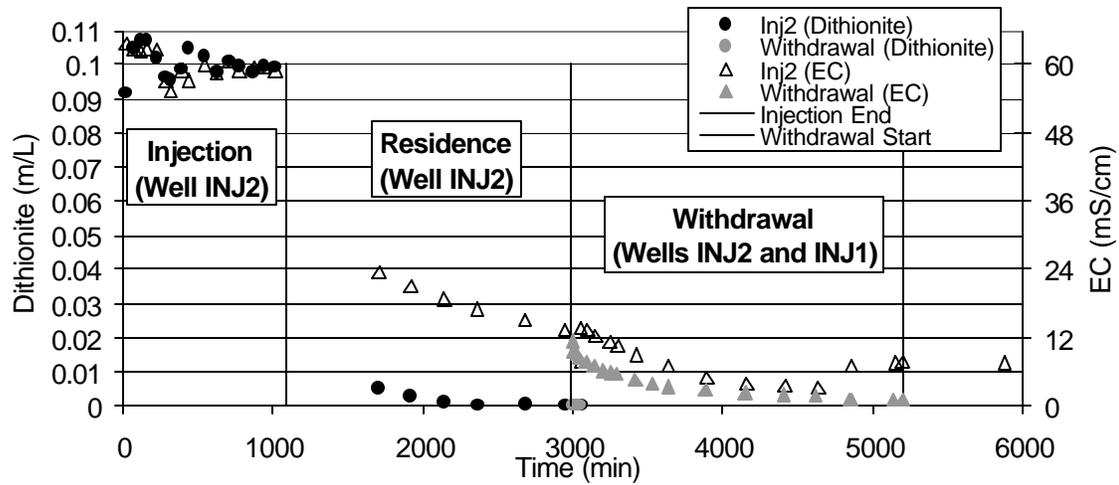


Figure 5.3. Dithionite and EC measurements of the Injection and Withdrawal streams during the FHC Pilot-Scale Dithionite Injection/Withdrawal Test.

6.0 Preliminary Performance Assessment

Preliminary performance assessment of the ISRM pilot test site is based on comparison of Cr(VI) concentrations within the treatment zone following emplacement of the reduced zone with pre-treatment baseline conditions. These Cr(VI) performance data are shown in Figures 6.1 and 6.2. As indicated, the preliminary results look promising. Hexavalent chromium concentrations have been reduced from as high as 4,500 µg/L to below detection limits (spectrophotometric method, 20 µg/L reported by EPA, 10 µg/L cited in manufacturer specifications) in all monitoring wells within the established treatment zone. It should be noted that MW-5 (along with the up- and down-gradient monitoring wells) should not be considered as located within the treatment zone due to the limited (or absence of) treatment at these wells. Due to project constraints, additional interpretation and reporting of performance measures (e.g., DO, ORP, trace metals concentrations) was not completed for inclusion in this letter report.

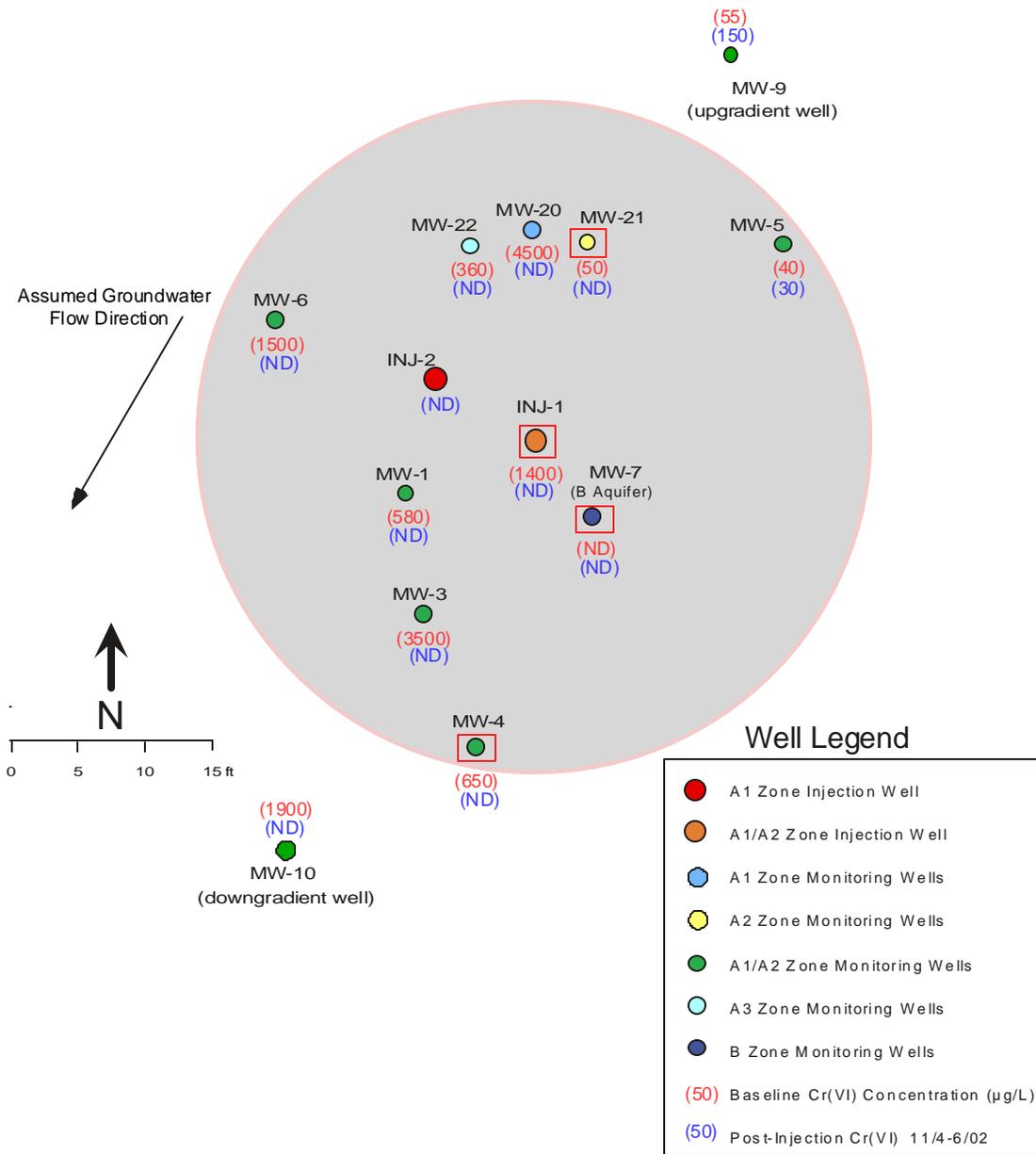


Figure 6.1 Comparison of Baseline Cr(VI) Concentrations with Measurements from the First Post-Emplacement Performance Assessment Sampling Event

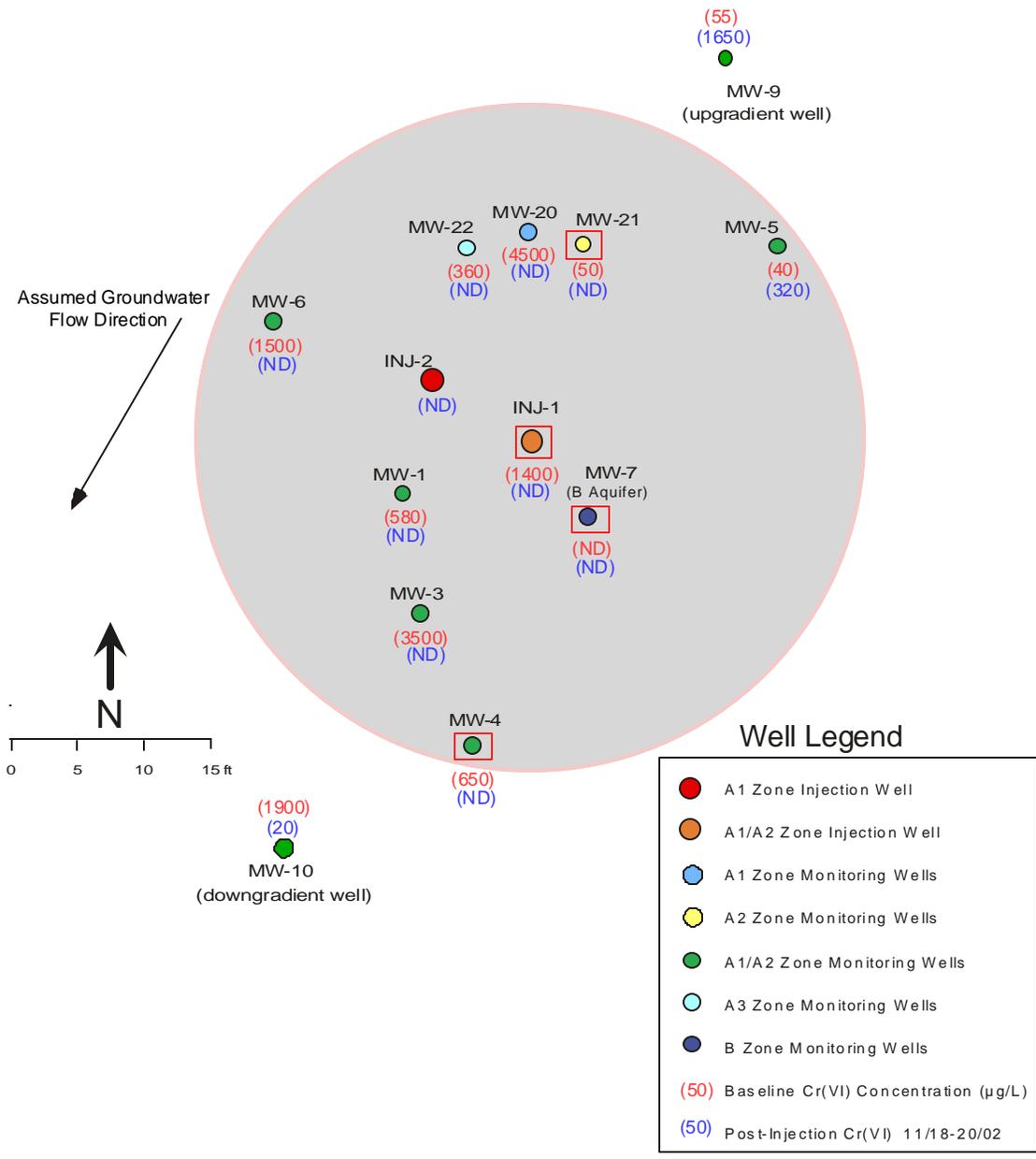


Figure 6.2 Comparison of Baseline Cr(VI) Concentrations with Measurements from the Second Post-Emplacement Performance Assessment Sampling Event

7.0 References

- Cinco, H., Samaniego, F., and Dominguez, N. Transient Pressure Behavior for a Well with a Finite Conductivity Vertical Fracture. Soc. Petr. Eng. J., (August 1978), 253-264.
- Cinco, H., Samaniego, F. Transient Pressure Analysis for Fractured Wells. J. Pet. Tech., (September 1981).
- Fruchter JS, FA Spane, JK Fredrickson, CR Cole, JE Amonette, JC Templeton, TO Stevens, DJ Holford, LE Eary, BN Bjornstad, GD Black, JM Zachara, and VR Vermeul. 1994. *Manipulation of Natural Subsurface Processes: Field Research and Validation*. PNL-10123, Pacific Northwest National Laboratory, Richland, Washington.
- Fruchter JS, JE Amonette, CR Cole, YA Gorby, MD Humphrey, JD Istok, FA Spane, JE Szecsody, SS Teel, VR Vermeul, MD Williams, and SB Yabusaki. 1996. *In Situ Redox Manipulation Field Injection Test Report - Hanford 100H Area*. PNNL-11372, Pacific Northwest National Laboratory, Richland, Washington.
- Fruchter, J.S., C.R. Cole, M.D. Williams, V.R. Vermeul, J.E. Amonette, J.E. Szecsody, J.D. Istok, and M.D. Humphrey. 2000. Creation of a Subsurface Permeable Treatment Barrier Using In Situ Redox Manipulation. Groundwater Monitoring and Remediation Review, spring 2000.
- Rai D., L.E. Eary, and J.M. Zachara. 1989. Environmental chemistry of chromium. Sci. Total Environ., 86, 15-23.
- Szecsody, JE, BJ DeVary, VR Vermeul, MD Williams, JS Fruchter. October, 2002. *In Situ Redox Manipulation Bench-Scale Tests: Remedial Design Support for ISRM Barrier Deployment, Frontier Hard Chrome Site, Vancouver, Washington*. Letter Report to EPA. Pacific Northwest National Laboratory, Richland, WA.
- Szecsody, J., M. Williams, J. Fruchter, V. Vermeul, and J. Evans. 2000. Influence of sediment reduction on TCE degradation, remediation of chlorinated and recalcitrant compounds, book chapter, ed. G. Wickramanayake, *Chemical Oxidation and Reactive Barriers*, p. 369-376.
- Vermeul, V.R., S.S. Teel, J.E. Amonette, C.R. Cole, J.S. Fruchter, Y.A. Gorby, F.A. Spane, J.E. Szecsody, M.D. Williams, and S.B. Yabusaki, 1995, *Geologic, Geochemical, Microbiologic, and Hydrologic Characterization at the In Situ Redox Manipulation Test Site*; PNL-10633; Pacific Northwest Laboratory, Richland, Washington.
- Vermeul, V.R., M.D. Williams, J.C. Evans, J.E. Szecsody, B.N. Bjornstad, and T.L. Liikala. 2000. *In Situ Redox Manipulation Proof-of-Principle Test at the Fort Lewis Logistics Center*. PNL-13357, Pacific Northwest Laboratory, Richland, Washington.

Vermeul VR, Williams MD, Szecsody JE, Fruchter JS, Cole CR and Amonette JE. 2002. "Creation of a Subsurface Permeable Reactive Barrier Using In Situ Redox Manipulation". in *Groundwater Remediation of Metals, Radionuclides, and Nutrients with Permeable Reactive Barriers*. (book):163. Academic Press, San Diego, CA

Williams, M.D., S.B. Yabusaki, C.R. Cole, and V.R. Vermeul. 1994. In Situ Redox Manipulation Field Experiment: Design Analysis". pub in *In Situ Remediation: Scientific Basis for Current and Future Technologies*, p. 1131-1152. ed. by G.W. Gee & N.R. Wing, pub. by Battelle Press, Columbus, Ohio.

Williams MD, VR Vermeul, JE Szecsody, JS Fruchter, and CR Cole. 1999a. *100-D Area In Situ Redox Treatability Test for Chromate-Contaminated Groundwater: FY 1998 Year-End Report*. PNNL-12153, Pacific Northwest National Laboratory Richland, Washington.

Williams MD, VR Vermeul, M Oostrom, JC Evans, JS Fruchter, JD Istok, MD Humphrey, DC Lanigan, JE Szecsody, MD White, TW Wietsma, and CR Cole. 1999b. *Anoxic Plume Attenuation in a Fluctuating Water Table System: Impact of 100-D Area In Situ Redox Manipulation on Downgradient Dissolved Oxygen Concentrations*. PNNL-12192, Pacific Northwest National Laboratory, Richland, Washington.

Williams MD and M Oostrom. 2000. "Oxygenation of anoxic water in a fluctuating water table system." *Journal of Hydrology*, 230:70-85.

Williams M.D., V.R. Vermeul, J.E. Szecsody, and J.S. Fruchter. 2000. *100-D Area In Situ Redox Treatability Test for Chromate-Contaminated Groundwater*. PNNL-13349, Pacific Northwest National Laboratory, Richland, Washington.