

Test Plan

In Situ Redox Manipulation Bench- and Pilot-scale Tests: Remedial Design Support for ISRM Barrier Deployment

Frontier Hard Chrome Superfund Site
Vancouver, WA

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Appendix A: Sampling and Analysis Plan

1.0 Introduction

This report describes the proposed In Situ Redox Manipulation (ISRM) Bench and Pilot Tests for the treatment of hexavalent chromium in the groundwater at the Frontier Hard Chrome (FHC) site, Vancouver, Washington. The scope of this document covers the test objectives, bench-scale testing, field activities, and project controls for the ISRM Pilot Test. The test will be conducted as a Treatability Test under the provisions of CERCLA.

1.1 Objective

The objective of the In Situ Redox Manipulation Pilot Test is 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, 1999) with very 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 this test will be used to determine the feasibility of, and develop the remedial design for, a potential full-scale ISRM barrier at this location.

1.2 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., in press). 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.

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, HCrO_4^-) 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.

1.3 Site Description

The Frontier Hard Chrome (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. 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 source areas, and a long-term treatment barrier for any residual contaminant leaching, should it occur.

1.3.1 Site Hydrogeology

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-foot-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 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 5 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.

The potentiometric surface is relatively flat across the inactive floodplain on which the Frontier Hard Chrome site is located. 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.

1.4 Test Summary

As discussed previously, the bench- and pilot-scale testing program covered by this test plan is designed to determine the feasibility of, and develop a remedial design for, a potential full-scale ISRM barrier for the remediation Cr(VI) contaminated groundwater at the FHC site. Because this testing is being conducted as part of the remedial design, the barrier location has not yet been finalized. However, based on currently available information, an approximate location has been identified (Figure 2). The final ISRM barrier location/orientation will be based on the determined design of the source term shallow soil mixing treatment extent, the natural groundwater flow direction at the site, and site access considerations. The ISRM barrier will be located downgradient of the source term area and be oriented to intercept contaminants mobilized during the source term treatment and provide additional long-term protection of groundwater in the event any residual contaminant leaching occurs.

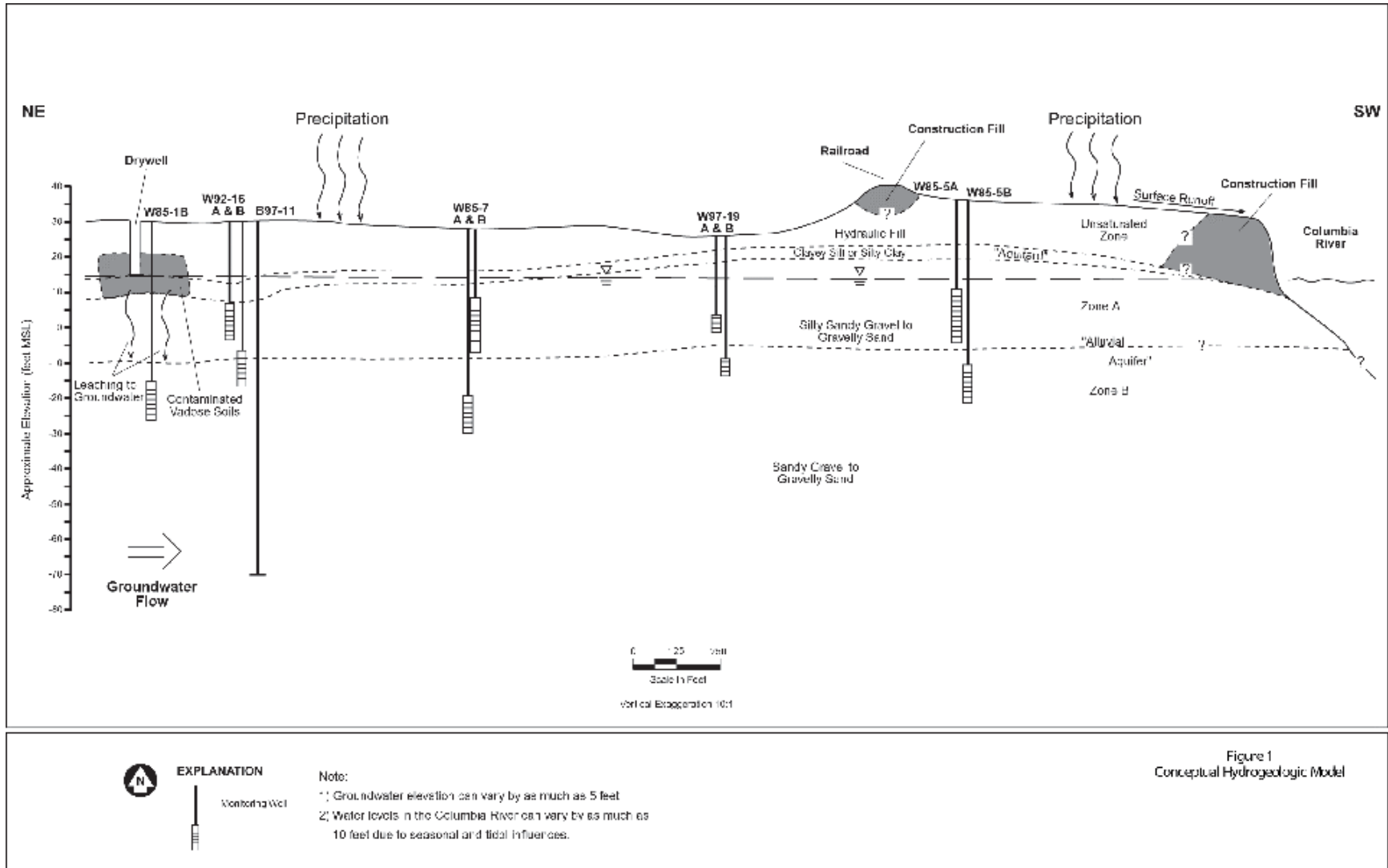
The ISRM pilot test site will be located somewhere along the length of the anticipated ISRM barrier location. One injection/withdrawal well and 8 monitoring wells will be installed to monitor the injection tests as shown in Figure 3. If possible, one upgradient and one downgradient well should also be installed. Although demonstrating the performance of a pilot-scale ISRM treatment zone using upgradient and downgradient monitoring data, which is not a primary objective of this field testing program, can be difficult unless the groundwater flow direction is well understood, these wells would provide useful supplemental data and will eventually be needed when the ISRM barrier is installed.

Sediment samples will be collected during the installation of selected wells (as indicated in Figure 3) for laboratory analysis of physical and geochemical properties (bench-scale testing is discussed in Section 2). Following well completion and initial well development, at least one set of baseline groundwater samples will be collected from all wells installed at the ISRM pilot test site to establish pre-test (baseline) conditions. Once

baseline conditions have been established, characterization activities (hydraulic testing and a tracer injection test) will be conducted to provide hydrogeologic data needed to design the dithionite injection/withdrawal test. The dithionite injection/withdrawal test will be conducted by injecting a solution containing sodium dithionite and a potassium carbonate/bicarbonate pH buffer into the central injection/withdrawal well shown in Figure 3. Additional time will be provided after the injection period for reactions with the sediment and dithionite to proceed. Unless the EPA determines the cost of recovering residuals is not warranted for the benefits realized, unused reagent and reaction products will then be withdrawn from the aquifer by pumping from the central injection/withdrawal well.

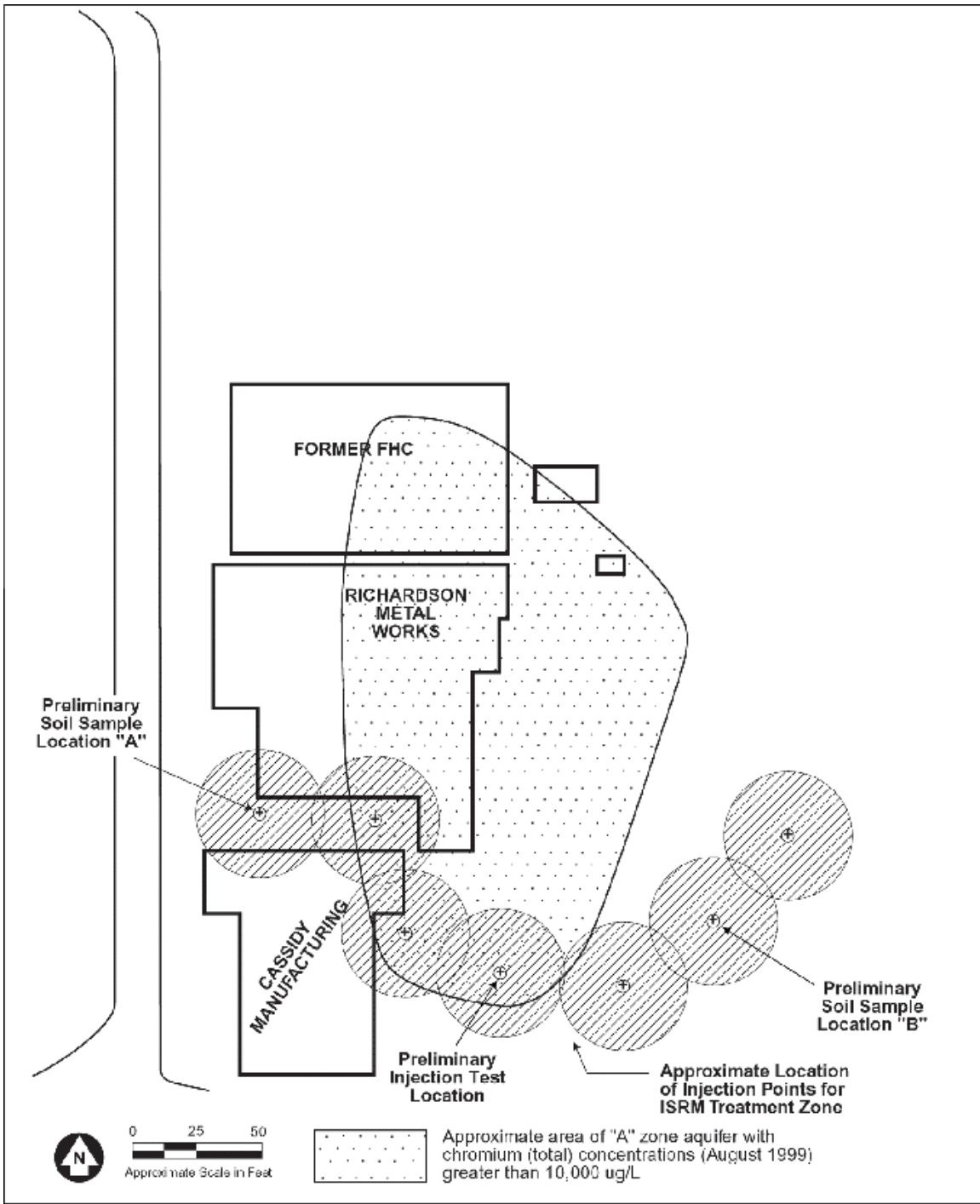
Following the pilot-scale dithionite injection test, groundwater samples will be collected and analyzed from all ISRM pilot test site monitoring wells to assess barrier performance by comparing post injection hexavalent chromium concentrations with the baseline concentrations. Although analysis of aqueous samples from the site provides indirect evidence of the reduction of aquifer sediments (i.e., dissolved oxygen and Cr(VI) concentrations), direct measurement of the reduction of the aquifer sediment is only possible through the analysis of sediment samples collected from borings drilled at the site following the dithionite injection test. Pre-injection sediment samples will be collected and analyzed for available iron as part of this ISRM remedial design testing program. These data, in addition to providing information needed to design the dithionite injection, can be used to provide an estimate of the ISRM treatment longevity. However, these longevity estimates are based on laboratory conditions and do not take into account the efficiency of the field-scale reduction. Direct measurement of post-injection reductive capacities is not included in the scope of this field testing program but should be considered during the remedial action phase of this project. Samples could be collected during the barrier expansion drilling campaign and submitted for laboratory analysis to determine the field achieved reductive capacity of the sediments at the FHC site.

This ISRM Pilot Scale Field Test Plan includes a description of the bench-scale tests that will be conducted on sediment samples from the targeted ISRM treatment zone (samples will be collected by EPA) to determine physical and geochemical properties relevant to the ISRM process (Section 2), a description of field activities for site characterization and creation of the pilot scale ISRM treatment zone (Section 3), a discussion of sampling and analysis requirements (Section 4 and Appendix A), and a brief discussion of data management/reporting and health and safety training requirements (Sections 5 and 6, respectively) and a tentative schedule for field activities (Section 7).



06-16-10, Fig 1.1

Figure 1. Site Conceptual Hydrogeologic Model



EPA REGION 10

Figure 2
ISRM Treatment Barrier

02-0160 Fig2.ai

Figure 2. Site Map Showing the Approximate Locations of the Source Term Shallow Soil Mixing Area and the ISRM Barrier Location



Figure 3. ISRM Pilot Test Site Well Layout and Sediment Sample Collection Locations

2.0 Bench-Scale Testing

Laboratory scale studies of dithionite interactions with FHC sediments will be conducted on samples provided by the EPA. The specific objectives of this study are: a) determine the average reducible iron content of sediments in the barrier zone at the site, b) quantify the Frontier sediment reduction rate by sodium dithionite, and c) assess the spatial variability of the reducible iron content. This geochemical information needed for designing the pilot-scale ISRM injection test, developing the remedial design of the full-scale ISRM barrier, and providing an initial assessment of barrier longevity. Additional secondary parameters that will be measured include: a) dry bulk density, b) porosity in a packed column, and c) mass of sediment < 4 mm. While a previous laboratory-scale study (Szecsody, 1999) concluded that there was sufficient reducible iron in some FHC sediments (0.22% to 0.37%), sediments specifically from the A Aquifer at the pilot test site were not studied.

2.1 Mass of Reducible Iron

The mass of dithionite-reducible iron in FHC sediments will be assessed by laboratory flow experiments in which sediments are reduced then oxidized. The dithionite chemical treatment dissolves and reduces amorphous and some crystalline Fe(III) oxides. The reduced Fe(II) created by the dithionite chemical treatment appears to be present in several different Fe(II) phases: adsorbed Fe(II), Fe(II)-carbonate (siderite), and FeS (iron sulfite), although adsorbed Fe(II) appears to be the dominant Fe(II) phase. The mass of reducible iron will be calculated using reduction experimental data (experiments described below) from the dithionite mass loss in excess of disproportionation. The mass of reducible iron will be additionally calculated during sediment oxidation experiments, in which dissolved oxygen in water is reacted with reduced sediment and the mass of oxygen consumption is determined. These oxidation experiments (described below) are considered the most accurate method (Szecsody et al., 2000), as only one reaction (oxidation) is occurring, as opposed to several reactions during reduction experiments (iron oxide dissolution, reduction, and disproportionation). For this study, two sediment samples will be used for reduction and oxidation column experiments. One sediment will be from the injection well, and the other sediment will be a physical mixture of sediments from all boreholes to produce an average, composite sample.

Sediment reduction studies will be conducted in 1-D columns and will consist of injecting the dithionite solution at a steady rate into a sediment column and measuring the concentration of dithionite over time in the effluent for 48 to 160 h. The flux rate will be chosen to achieve specific residence times of the dithionite solution in the column (2 h to 4 h) relative to the reduction rate (~5 to 7 h). The dry bulk density and porosity of the column will be calculated from the dry and saturated column weight and column volume. The volumetric flow rate will be calculated from the effluent volume and elapsed time. The electrical conductivity of the column effluent provided a second (dynamic) measure

of the porosity, and will be measured using a flow-through electrode and automatic data logging.

Sediment oxidation studies will be conducted in 1-D columns to determine the rate at which the dithionite-reduced sediments are oxidized and to measure of the mass of reduced iron (i.e., redox capacity). These experiments will consist of injecting oxygen-saturated (8.4 mg L^{-1}) water at a steady rate (typically 2 pore volumes per hour) into a reduced sediment column and measuring the concentration of dissolved oxygen over time in the effluent for 100 to 800 h. A series of in-line micro-electrodes will be used to monitor geochemical changes during oxidation and include dissolved oxygen (2 electrodes), Eh, pH, and electrical conductivity. Electrode measurements are continuously monitored, averaged, and data logged at 2 to 5 minute intervals. Two point calibration are conducted on the in-line oxygen electrodes at 4 - 8 h intervals (oxygen-free and oxygen-saturated solution for oxygen) using an automated fluid system. Electrode data from calibrations are also data logged. The mass of reduced iron that is oxidized is calculated from the mass of oxygen consumed.

2.2 Rate of Iron Oxide Reduction by Dithionite

The rate of reduction of iron oxide phases in the FHC sediments will be quantified by batch studies in which the rate of dithionite consumption is monitored over time. These batch studies will be conducted on two sediments: the injection well, and a mixture of barrier area sediments. These batch experiments will consist of a single large septa-top glass bottle in which 14 g to 200 g of sediment is mixed with the dithionite solution for hundreds of hours. The experiment is then mixed on a linear shaker at slow rpm (to not cause particles to break up) and placed in a temperature-controlled chamber (25°C). At specific time intervals (minutes to tens of hours, a sample was withdrawn, filtered, and analyzed for dithionite remaining in solution. It is assumed that the sample volume withdrawn (0.2 mL) is small relative to the total system volume, and so the sampling will not affect the experimental conditions. The dithionite solution will contain 0.001 mol L^{-1} to 0.10 mol L^{-1} sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), with 4x the dithionite concentration K_2CO_3 , and 0.4x KHCO_3 . These batch experiments will be conducted inside an anaerobic chamber to prevent the dithionite from reacting with oxygen. The dithionite concentration will be measured by UV absorption at 315 nm, as described below. The rate of dithionite reduction (and rate of disproportionation) can be quantified from the experimental data by using a reaction simulator of these reactions.

The dithionite concentration in these batch experiments and in the effluent from the previously described column experiments will be measured once per hour using an automated fluid system and data logging equipment. These measurements are taken with an HPLC injection valve with $15 \mu\text{L}$ to $52 \mu\text{L}$ loop that isolates a specified volume of the effluent. The contents of the loop are mixed with 5 mL to 10 mL of oxygen-free water, then injected into a UV-detector and absorbance measured at 315 nm. The sample injection takes 2 minutes to flow the complete sample through the detector, and the absorbance over a 1-minute interval are averaged for a single dithionite concentration

measurement. A triple-wash between injections prevents sample overlap. These fluid operations are controlled from one computer, and the dithionite concentration logged on a second computer. In the column experiments, the concentration of the dithionite influent are also measured with the same automated system by manually bypassing the column at approximately 24 h intervals over the multi-day experiments. The fraction of reduced iron is calculated from dithionite breakthrough curves by determining the total mass loss (i.e., dithionite mass injected minus dithionite in the effluent) and the mass of dithionite used for disproportionation. The remaining dithionite mass loss is consumed by iron reduction. This dithionite breakthrough analysis assumes that dithionite has reached a steady state mass loss due to disproportionation and that all the iron has been reduced. The rate of iron reduction is also calculated from the steady state dithionite concentration during initial breakthrough (i.e., before the iron is all reduced).

2.3 Spatial Variability of Reducible Iron Mass

The mass of reducible iron can be most accurately measured by column oxidation experiments (described above), although these automated experiments take 2 to 4 weeks each. These tests are intrinsically accurate, as they simulate the natural oxidation process in the subsurface: dissolved oxygen in water is slowly oxidizing reduced ferrous iron phases. Iron extractions of reduced sediments have been used in other laboratory studies to quantify some of the reduced iron oxide phases (i.e., decrease in Fe(III) phases, increase in Fe(II) phases) that result from dithionite treatment of sediments. While the exact Fe(II) phases that are extracted are somewhat operational and do not represent the same total mass as what is reduced by dithionite treatment, the spatial variability of the extraction masses can be used to quantify the spatial variation in iron geochemistry in the sediments. Iron extractions conducted on untreated and dithionite-treated sediments in an anerobic chamber will consist of: a) 1 M CaCl_2 (Fe^{II} ion exchangeable), b) 0.5 M HCl (total ferrous; Heron et al., 1994). These aqueous solutions are reacted with reduced sediments for 48 h, then the aqueous Fe^{II} and Fe^{III} solubilized from sediments into solution are quantified by ferrozine. For this study, approximately 10 sediment samples (i.e., from different wells and different depths within the same well) will be used for this spatial variability assessment. The two sediment samples (injection well, mixed sediment) used in other studies will also be used, so that the percentage of spatial variation can be scaled to the mass of reducible iron.

3.0 Field Activities

This section describes the approach and specific field activities planned for the ISRM pilot test. The field activities, purpose, and resulting data are outlined in Table 1. These activities are discussed in more detail in the following sections. The sampling and analysis Plan (SAP) contained in Appendix A describes the sediment and groundwater samples that will be collected during these field activities; also contained in the SAP is a discussion of the analysis methods and quality assurance requirements for this work scope. Details on the results of previous ISRM site characterization and emplacement activities are in Vermeul et al. (1995, 2000) and Williams et al. (2000).

Table 1 ISRM Pilot Test Field Activities

| Activity (resp) | Method | Results |
|--|---|--|
| Groundwater Gradient/flow Direction (Weston/EPA) | Measure water levels in wells in the area of selected site (including new wells installed below) | Water level maps showing groundwater flow direction and magnitude |
| Well Installation and development (EPA/Weston) | Geoprobe direct push and standard (hallow stem auger, cable tool, sonic) drilling with sediment sampling | Installation of Injection/Withdrawal and Monitoring wells. Hydrogeology of site. Sediment samples for physical and chemical properties (i.e., reducible iron content). |
| Baseline Groundwater Chemistry (EPA/Weston) | At least 1 complete set of measurements from all pilot test site wells; 3 sets preferable | Groundwater chemistry (Cr^{6+} , pH, ORP, EC, DO, Temp., Trace Metals, Anions) of site prior to ISRM treatment. |
| Site Setup (PNNL/Weston) | Mobilize injection and monitoring equipment and set up on site, site services | Injection and monitoring systems operational and ready for field tests |
| Aquifer Testing (PNNL) | Step injection test and short duration constant rate injection test | Injection and pumping rates, semi-quantitative estimates of hydraulic properties |
| Tracer Test (PNNL) | Injection tracer in central injection well with measurements in surrounding monitoring wells. | Arrival curves in monitoring wells to determine porosity of site and volumes/rates required for ISRM treatment. Pressure recovery monitoring will provide more quantitative estimate of hydraulic properties |
| Dithionite Injection / Withdrawal (PNNL) | Inject Sodium Dithionite, provide reaction time, recover residual | Arrival curves at monitoring wells. Effectiveness of dithionite treatment. Determine residuals and percentage of injected mass withdrawn. |
| Groundwater Monitoring (EPA/Weston) | Water sampling, field screening, and laboratory analysis from wells at site 3 sets from all pilot test wells. | Groundwater chemistry (Cr^{6+} , pH, ORP, EC, DO, Temp., Trace Metals, Anions) of site following to ISRM treatment. Ongoing for duration of project |

3.1 Determination of Hydraulic Gradient and Direction

Prior to initiation of drilling, water-level data will be collected and/or historic data will be reviewed from wells in the vicinity of the proposed ISRM pilot test site to determine the local groundwater gradient and flow direction. These data should be used by Weston/EPA to develop a current water table map that can be used to guide placement and orientation of the ISRM pilot test well layout. Water-level measurements should be collected over as short a time period as possible. Initial measurements should be rechecked throughout the measurement period to quantify any water-level changes due to external stress. These measurements, which should be repeated periodically and should include the newly installed wells once they are available, are needed to finalize the location and orientation of the full-scale ISRM barrier.

3.2 Well Installation

This section describes the field activities associated with the drilling, sampling, and completion of one injection well and up to 8 monitoring wells (Figure 3) within the A aquifer (Figure 1) at the site. Up to two monitoring wells will also be completed in the B Aquifer (below the A aquifer) for determination of reagent sinking during the injection/withdrawal tests and vertical Cr(VI) distribution. Since there are no well-defined aquitards between the A and B zone depth intervals, reagent sinking is an important aspect to understand and quantify. These wells will be used to support hydrogeologic characterization, design, emplacement, and performance assessment activities associated with the ISRM pilot field demonstration. The proposed location for the pilot field test site is shown in Figures 2 and 3 and Table 2 provides selected pilot test well specifications including proposed drilling method, nominal well casing/screen diameter, depth interval, and radial distance from the central injection well.

As indicated in Table 2, two separate drilling methods will be used. Monitoring wells installed within the A zone depth interval will be installed by EPA using the Geoprobe direct push method. Because a 2-in monitoring well is required for the monitoring equipment that will be used to collect aqueous samples during the ISRM remedial design testing program, geoprobe prepack wells screens will not be used. The current plan is to install standard 2-in PCV wire wrapped screens using the geoprobe method which will result in installations with no annular filter pack or annular seal. EPA is currently in the process of testing this well configuration in a formation similar to the FHC site. If this non-standard well installation results in unacceptable turbidity levels or if adequate well capacity is not achieved (i.e., the monitoring wells should produce at least 1 gpm), then standard 2-in wells will be installed.

Table 2. Selected ISRM Pilot Test Well Specifications

| Well ID | Drilling Method | Nominal Casing Diameter | Depth Interval | Radial distance from Injection Well (ft) |
|---------|-----------------|-------------------------|----------------|--|
| INJ-1 | Standard | 6-in | A zone | -- |
| MW-1 | Geoprobe | 2-in | A zone | 10 |
| MW-2 | Geoprobe | 2-in | A zone | 12 |
| MW-3 | Geoprobe | 2-in | A zone | 15 |
| MW-4 | Geoprobe | 2-in | A zone | 20 |
| MW-5 | Geoprobe | 2-in | A zone | 22 |
| MW-6 | Geoprobe | 2-in | A zone | 24 |
| MW-7 | Standard | 2-in | B zone | 7 |
| MW-8 | Standard | 2-in | B zone | 20 |
| MW-9 | Geoprobe | 2-in | A zone | 35 |
| MW-10 | Geoprobe | 2-in | A zone | 35 |

The 6-in diameter injection well installed across the A zone and the monitoring wells installed in the B zone depth interval will be installed using a standard drilling and completion approach; EPA will subcontract for these drilling services. Acceptable drilling methods include hollow stem auger, sonic, and cable tool; due to the nature of the ISRM technology, air rotary drilling will not be allowed. The Geoprobe direct push installation method should not be used for these wells because a larger diameter is required for the injection well and because the lack of a competent annular seal in wells extending to the B zone depth interval is both a monitoring concern and a potential preferential pathway for transport of the dense reagent to the deeper aquifer zone. All wells will be completed using PVC casing and PVC wire-wrapped screen.

One of EPA's characterization objectives of this drilling campaign is to better define the depth extent of contamination and any geologic controls that may contribute to the differences in contaminant distribution observed between the A and B aquifer zones. This will be accomplished by collecting groundwater samples at various locations and depths using the geoprobe direct push sampler and analyzing the samples in the field for Cr(VI). These data will be used to determine the targeted depth interval for the ISRM treatment zone, and subsequently, the screen interval for the injection well and surrounding monitoring wells. Figure 3 shows well locations within the pilot test site where sediment samples will be collected and Figure 1 shows the hydrogeologic conceptual model of the site.

During installation of the injection well and selected monitoring wells at the ISRM field test site, sediment samples will be collected by EPA and shipped to PNNL for laboratory analysis. For each A zone monitoring well indicated, a sediment sample will be collected from the top, middle, and bottom of the A zone depth interval. For each B zone monitoring well indicated, a sediment sample will be collected from the top, middle, and bottom of the A zone depth interval and a single sample will be collected from the B zone depth interval. In addition to samples collected at the ISRM pilot test site, sediment samples from the top, middle, and bottom of the A zone depth interval will also be collected from near the western and eastern extents of the anticipated full-scale barrier length. A detailed description of planned sediment sampling is contained in the Sampling and Analysis Plan (Appendix A).

Immediately following well completion, EPA will install an appropriately sized development pump in each well and conduct development pumping to remove fine-grained material mobilized/generated during drilling and test the hydraulic performance of each well installation. Development shall continue until the well is sufficiently developed as determined by an acceptable turbidity level and specific capacity for each well.

3.3 Baseline Groundwater Chemistry

From one to three sets of groundwater chemistry samples will be collected from site monitoring wells and submitted for analysis to establish baseline conditions, prior to the tracer test and emplacement of the ISRM treatment zone. Sampling and analytical equipment required for this activity will be supplied by EPA and will be capable of measuring the specific analytes indicated in Table A2 of the Sampling and Analysis Plan (Appendix A).

3.4 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.

3.4.1 Site Utilities

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

3.4.1.1 Water Supply

To conduct the tracer and dithionite injection tests, a substantial source of water is needed to make up the injection solutions. If a water supply is not available on site, groundwater can be withdrawn from wells prior to the test and stored in onsite storage tanks until the injection tests are conducted. At the FHC site, a nearby fire hydrant will supply the water needed for dilution of the concentrated tracer and dithionite solutions; each test will use over 40,000 gallons of water at rates as high as 90 gpm. Static pressure at the hydrant should be ~ 60 psi. Prior to the injection tests, water samples from the hydrant should be submitted for anions, trace metals, and chlorine analysis. For the tracer injection test, EPA or it's contractors will provide a tank of similar volume to the dithionite tanker (~6000 gal) for mixing the tracer solution.

3.4.1.2 Electrical Service

Electrical power is required to operate site facilities, including a mobile laboratory and associated analytical equipment, office/storage trailer, and injection/monitoring equipment. Site power can be

supplied by appropriately sized generators; however, line power is preferable because, once installed, it is virtually maintenance free and more reliable than generators.

3.4.1.3 Boiler

Because dithionite reaction rates are significantly reduced under relatively cold groundwater temperature conditions, a boiler may be used to preheat the aquifer prior to dithionite injection and to warm the injection solution during the injection phase. The water supply source (hydrant) would be warmed from its ambient temperature to an injection temperature of around 25°C using an oil-fired steam boiler. Design calculations indicate a 25 hp steam boiler would be capable of supplying the heat required to meet injection temperature specifications. A boiler unit used during a previous field test was rated at 862 lb steam/hour and fired on #2 fuel oil. The boiler was rated at 150-psi design pressure and was equipped with flame safeguard control, pressure operating controls, and low-water cutoff controls. Supply water was heated using a Bell and Gossett shell and tube heat exchanger. At high fire, the boiler consumed approximately 7.5 gallons of fuel per hour.

3.4.1.4 Wastewater Disposal

Due to the emplacement method planned for the ISRM pilot test at the FHC site (injection/withdrawal or push/pull), relatively large volumes of wastewater will be generated. EPA is currently considering its options for treatment/disposal of the generated wastewater.

3.4.2 Monitoring Equipment

3.4.2.1 Sampling Pumps

Dedicated Grundfos RediFlo2 sampling pumps will be installed in all site monitoring wells. The sample tubing from each of these sampling pumps will be routed inside an onsite mobile laboratory and connected directly to a sampling manifold. Sample pumps will be 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 multichannel interface (pump switch box) that allows multiple sample pumps to be operated using a single control box.

3.4.2.2 Sampling Manifold

A project-developed sampling manifold allows all sampling streams to be routed into a central manifold for monitoring field parameters (in a flow-through monitoring assembly) and collecting groundwater samples. 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.

3.4.2.3 Field Parameter Measurements

Field parameters will be monitored using pH, ORP, temperature, electrical conductivity, and dissolved oxygen electrodes installed in a flow-through monitoring assembly. The flow-through assembly has been 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 will be determined by monitoring stabilization of field parameters. The field parameter monitoring electrodes that will be used during this field test will meet the specifications shown in Table 3.

3.4.2.4 Field Parameter Verification

Field parameters will also be monitored on a separate verification station consisting of a system using micro-flow-through electrodes and a syringe pump.

Table 3. 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 |

3.4.2.5 Water-Level/Pressure Response Measurements

Pressure transducers (10 and 20 psi, 0.1% of full scale accuracy) will be installed in selected wells to monitor pressure response during hydraulic and dithionite/tracer injection tests and continuously recorded using a Campbell Scientific CR10 datalogger. Transducer readings will be validated periodically with water level measurements to check for transducer drift. Water levels will be 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.

3.4.3 Analytical Measurements

A comprehensive series of analytical measurements will be made throughout the project in support of the field objectives. These included measurements made in the field in an onsite trailer-based mobile laboratory during the injection/withdrawal tests or during sample collection for groundwater monitoring. Some samples will also be submitted to the EPA Manchester Laboratory for analysis.

During the injection/withdrawal activities, dithionite measurements will be performed in the mobile laboratory using an ultraviolet absorption system with an on-line automatic dilution capability. Field measurement of dithionite are needed because of the inherent instability of that reagent, rendering analysis in an offsite laboratory impractical. Dithionite calibration standards will be freshly prepared in the field from pure reagent materials.

Trace metal samples will be collected in 25-mL acid washed plastic vials. Concentrated Ultrex nitric acid will be included in each vial as a preservative. Baseline and performance assessment trace metals samples will be analyzed by inductively coupled plasma-mass spectrometry (ICP-MS; EPA 6020). Withdrawal samples will also be analyzed for total sulfur by inductively coupled plasma-optical emission spectroscopy (ICP-OES; EPA 6010). Ion chromatography will also be performed on unpreserved samples collected in 20-mL plastic vials using EPA Method 300.0.

3.4.4 Injection and Withdrawal Equipment

3.4.4.1 Injection Manifold

The injection manifold (Figure 4) consists 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 will be constructed of 316 stainless steel and will use stainless steel ball valves for both diversion/shutoff and flow control valves.

3.4.4.2 Injection Pump

A 0.75 hp Grundfos stainless steel multi-stage centrifugal pump (Model # CRN2-30) or comparable will be used for injecting the concentrated solution. The injection tubing that extends from the well-head to the center of the injection interval will be constructed of 1.5-in.-diameter stainless steel or PVC pipe.

3.4.4.3 Fluid Metering Pump

If the reagent is heated to increase reaction rates, a pre-heat phase may be used to warm up the aquifer grains prior to initiation of the dithionite injection. During the pre-heat phase, a fluid metering pump made by FMI Inc. (QD-2) would be used to meter a small amount of dithionite (~150 mL/min) into the injection stream to remove any dissolved oxygen from the warm water injection stream.

3.4.4.4 Turbine Flow-Meters

Omega turbine flow meters will be installed to measure the flow rate of the various streams and the total injection flow rate. Depending on the design injection rate, either a 1-in or 2-in. diameter flow meter will be used to monitor the dilution water and total injection rate and a 1-in. diameter flow meter will be used to monitor the injection rate of the concentrated tracer/dithionite solutions. These flow meters will be continually logged with a Campbell Scientific CR10 datalogger.

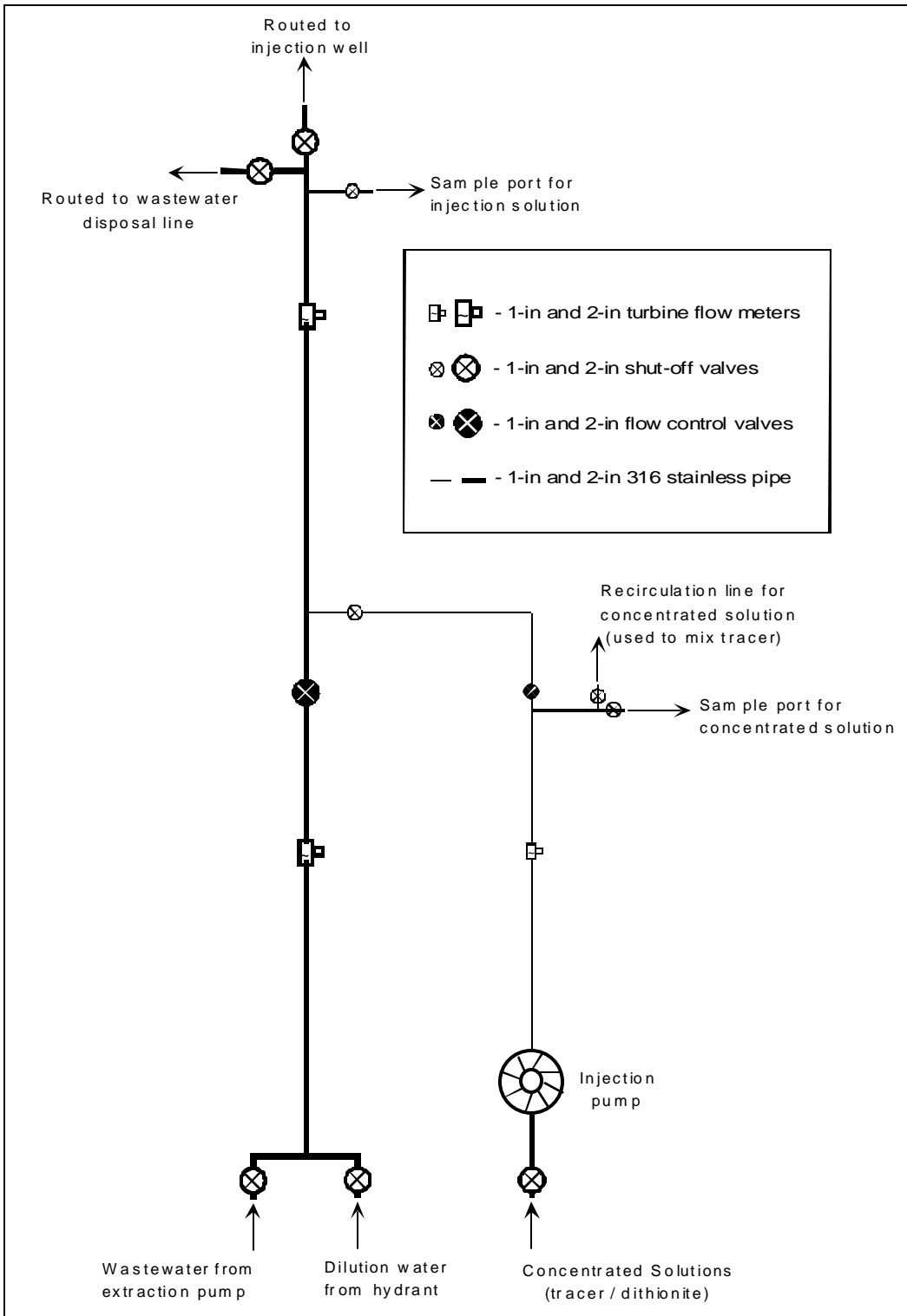


Figure 4. Schematic Drawing of the Tracer and Dithionite Injection System

3.4.4.5 Submersible Extraction Pump

An appropriately sized stainless steel submersible will be used as the extraction pump during the withdrawal phase of the test. The extraction pump will be installed on a 2-in.-diameter stainless steel riser.

3.4.5 Description of Equipment Integration/Operation

The following is a description of how the various equipment components were integrated into the systems required to conduct the tracer and ISRM injection tests at the FHC pilot test site.

3.4.5.1 Tracer and Dithionite Injection

The tracer and dithionite injection tests will be conducted using the equipment described above and illustrated in Figure 4. The desired injection concentration will be 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 will be provided by the stainless steel injection pump and the pressurized water supply (e.g., fire hydrant), respectively. The two injection streams will be mixed within the injection manifold before the solution arrives at the point of injection (i.e., the center of the injection well's screen interval). Supply water from the hydrant may be routed through the heat exchanger and raised to the desired temperature before entering the injection manifold.

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

Following the injection and residence phases of the test, remaining dithionite and reaction products may be extracted through the central injection/withdrawal well using a submersible extraction pump. Wastewater generated during the withdrawal phase will be routed back through the injection manifold to a wastewater disposal line that discharges to an approved disposal facility. Withdrawal water will be routed back through the injection manifold so that the same flow monitoring and control equipment used to monitor/control the injection can be used to monitor/control the withdrawal.

3.4.5.2 Groundwater Sample Collection

Groundwater sample collection will be conducted using the equipment described in Section 3.4.2 and illustrated in Figure 5. 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.

The procedure for monitoring field parameters and collecting groundwater samples using this equipment is described below:

1. Select well to be sampled on pump switch box and sampling manifold.
2. Move starter switch on variable speed control box to the start position. Pump frequency was preset to provide a purge rate of approximately 3 gpm.
3. Following displacement of any air bubbles trapped in the sample tubing (generally within the first 20 to 30 seconds), divert approximately 1 gpm of sample stream to flow-through monitoring assembly.
4. Monitor field parameters until they have stabilized. .
5. Record field parameter measurements and collect required groundwater samples; for selected cases collect an additional 10 mL syringe sample for field parameter verification on the micro-electrode station.

Select next well to be sampled and repeat process.

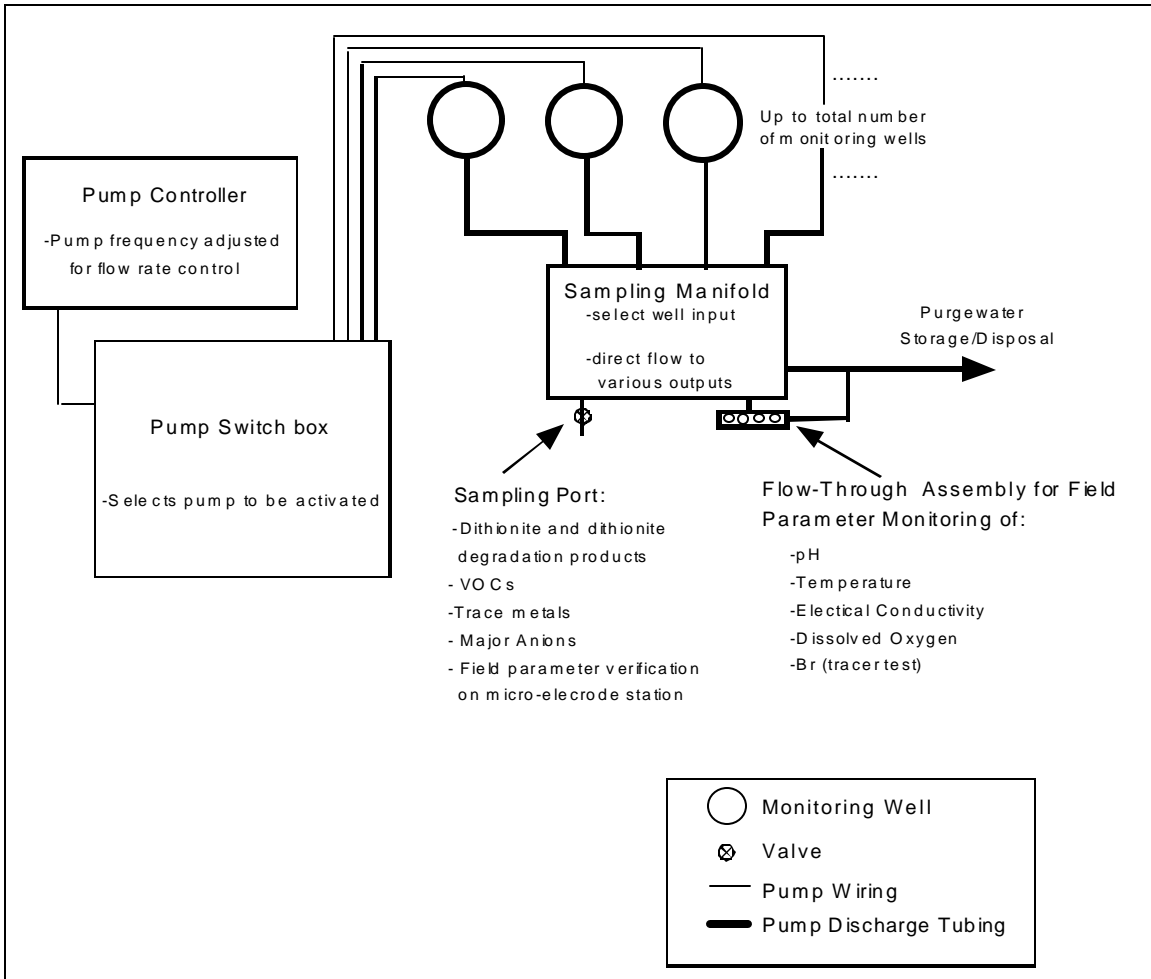


Figure 5. Schematic Drawing of the Groundwater Sample Acquisition System

3.5 Hydraulic Testing

Hydraulic tests will be conducted in the injection well and monitoring wells, as required, to determine the hydraulic properties of the aquifer and the specific capacity of the injection well prior to emplacement of the ISRM treatment zone. Due to schedule, budget, and waste disposal limitations, this initial hydraulic testing will be limited to a step injection test to determine the specific capacity of the injection well and a short duration constant-rate injection test to provide a semi-quantitative estimate of hydraulic properties. Pressure recovery data from the tracer injection test may also be analyzed if the short duration constant-rate injection test does not provide sufficient data for a good quantitative estimate of hydraulic properties. These test data will be representative of baseline (pre-injection) aquifer conditions and will be incorporated into the design analysis of the pilot technology demonstration.

Hydrologic test data will be analyzed using peer reviewed analytical or numerical methods that are applicable to the given test conditions.

3.6 Tracer Test

The objective of the tracer test is to help design and conduct the dithionite injection / withdrawal test (Section 3.7). This tracer test will provide information on the effective porosity of the pilot test site aquifer and arrival times at the monitoring wells. The effective porosity will help determine the volumes of dithionite solution required. The arrival curves will help design the sampling frequency needed for each monitoring well for the dithionite injection/withdrawal test. An additional benefit of the tracer test is to help test equipment operation and procedures needed for the dithionite injection/withdrawal test.

A solution containing the conservative tracer, potassium bromide (KBr, 100 ppm Br-), will be prepared and injected into the central injection/withdrawal well shown on Figure 3. Bromide concentrations will be measured in the surrounding monitoring wells and breakthrough curves (time vs. concentration) will be prepared for each well. The volume of tracer solution required, which will be similar to the nominal injection planned for the ISRM pilot test, will be dependent on the targeted treatment zone thickness at the test site. The source of injection water for this test will be from the local water supply system (or alternative source). The injected tracer will not be withdrawn during this test.

Bromide concentrations will be measured using ion-specific electrode at the field site (see Table 4 in Appendix B). Archive samples will also be collected and submitted to EPA laboratories for verification by ion chromatography

3.7 Dithionite Injection / Withdrawal Test

The objective of the dithionite injection/withdrawal test is to create a reducing zone to treat hexavalent chromium contamination migrating through the zone under natural gradient conditions. This test consists of three stages: Injection, Reaction, and Withdrawal. The reagent is injected into the aquifer in the central injection/withdrawal well (Figure 3) during the Injection stage and allowed to react with the aquifer sediments during the Reaction stage. This is followed by the Withdrawal stage where the unused reagent, reaction products, and degradation products are withdrawn from the aquifer using the central injection / withdraw well.

3.7.1 Injection Stage

Sodium dithionite is the reducing agent used to reduce the Fe(III) in the sediments to Fe(II). A potassium carbonate/bicarbonate pH buffer will be added to the reagent to enhance dithionite stability. The actual concentrations used in the test will be based on the results of laboratory tests on the available (e.g., reducible) Fe(III) in the sediment by the dithionite treatment method (see Section 2 and Szecsody et al., 1999).

An estimated 40,000 gallons of reagent will be required for the dithionite injection. The actual volumes and injection rates used for this test will be determined by the results of the bench-scale tests and the tracer test. During all stages of the test, aqueous samples will be collected from the injection solution and monitoring wells for field measurement of dithionite, pH, electrical conductivity, dissolved oxygen, and ORP (See Table 4 in Appendix A). Archive samples will also be collected for trace metals and anions analysis on selected samples.

The injection solution will be prepared using a concentrated solution delivered to the site in a tanker truck (~ 6000 gallons) and diluted with water using a local water source (i.e., local water supply or on-site storage tanks). Pumps and flow meters will be used to accurately mix the solution to the design concentration "in-line" prior to injection.

3.7.2 Residence Stage

A residence stage of up to 2 days is required to provide time for any remaining dithionite to react with remaining Fe(III) when the injection period is over. Aqueous sampling will also be conducted during this stage of the test.

3.7.3 Withdrawal Stage

Unless the EPA determines the cost of recovering residuals is not warranted for the benefits realized, unused reagent and reaction products will be withdrawn from the aquifer by pumping from the central injection/ withdrawal well. A description of the advantages and disadvantages associated with not withdrawing the spent reagent and reaction products is included below:

- Advantages
 - Eliminates wastewater disposal requirements (up to 200,000 gal)
 - Shortens duration of pilot test
 - Cost savings

- Disadvantages
 - No data collected on residuals recovery
 - The large quantity of reduced sulfur species left in the aquifer could lead to the growth of sulfur-reducing bacteria and potentially, sulfide production
 - The spent reagent plume is high pH/alkalinity with elevated and mobile trace metals (e.g., As, Fe, Mn); Additionally, the high alkalinity could lead to carbonate precipitation
 - The high density of the solution will cause it to sink to the B zone depth interval where it may be hard to recover

Based on these factors and criteria developed by the EPA for residual chemicals in the aquifer following the ISRM pilot test, up to five injection-volumes will be withdrawn from the aquifer. Given the instability of dithionite, and rapid reaction with dissolved oxygen, the reaction and degradation products of the reagent eventually degrade or oxidize to sulfate. In addition, trace metals and iron and manganese may be elevated in the withdrawn water due to dissolution of naturally-occurring co-precipitated metals within the iron oxides in the sediment. Aqueous sampling from the withdrawn water will also be used to estimate the percentage of the injected reagent that was withdrawn and the amount of residuals in the aquifer.

The withdrawn water from the ISRM Pilot test will be disposed of, as directed by the EPA, to an approved disposal facility. Required estimates of the concentrations of constituents in the withdrawal water will be submitted to EPA prior to disposition to the disposal facility.

3.8 Performance Assessment Monitoring

Post-injection performance assessment groundwater samples will be collected from the site by EPA and analyzed for hexavalent chromium and other constituents as listed in the Sampling and Analysis Plan (Appendix A). Three sets of groundwater chemistry samples will be collected from all pilot test site monitoring wells and submitted for analysis to assess the performance of the pilot injection test. Samples will be collected two weeks, one month, and two months after the injection,. Additional groundwater sampling will be conducted as required for the duration of the project and subsequently will be replaced by compliance monitoring of the full-scale ISRM barrier installation.

4.0 Sampling and Analysis

As discussed in the previous sections, aqueous and sediment sampling will be conducted throughout the various stages of the ISRM remedial design testing program. All sampling will be conducted in accordance with the Sampling and Analysis Plan (Appendix A) and investigation derived waste will be handled in accordance with EPA requirements. The EPA will assume ownership of all derived wastes; PNNL will not be responsible for any costs associated with the final disposal of sediment or aqueous samples. With the exception of aqueous samples submitted to the EPA Manchester Laboratories for analysis, all aqueous samples will remain on the FHC site and will be disposed of in accordance with EPA requirements. Sediment samples from the bench-scale testing will be shipped back to the FHC site prior to project completion for final disposal.

5.0 Data Recording / Management / Reporting

Drilling, completion, and sampling activities shall be recorded on the applicable procedural forms or logbooks and maintained in the field files by the EPA project personnel. Upon completion of all activities, the field file custodian shall transmit a copy of all well drilling, completion, development, and sampling documentation to PNNL for inclusion in the project files.

For the tracer and dithionite injection tests associated with this ISRM remedial design testing program, a project specific database will be developed and maintained to collect, organize, store, verify/validate, and manage analytical laboratory data and/or field measurements for collected samples. The data will be stored electronically in Microsoft Excel spreadsheets and paper copies will be maintained in the project files.

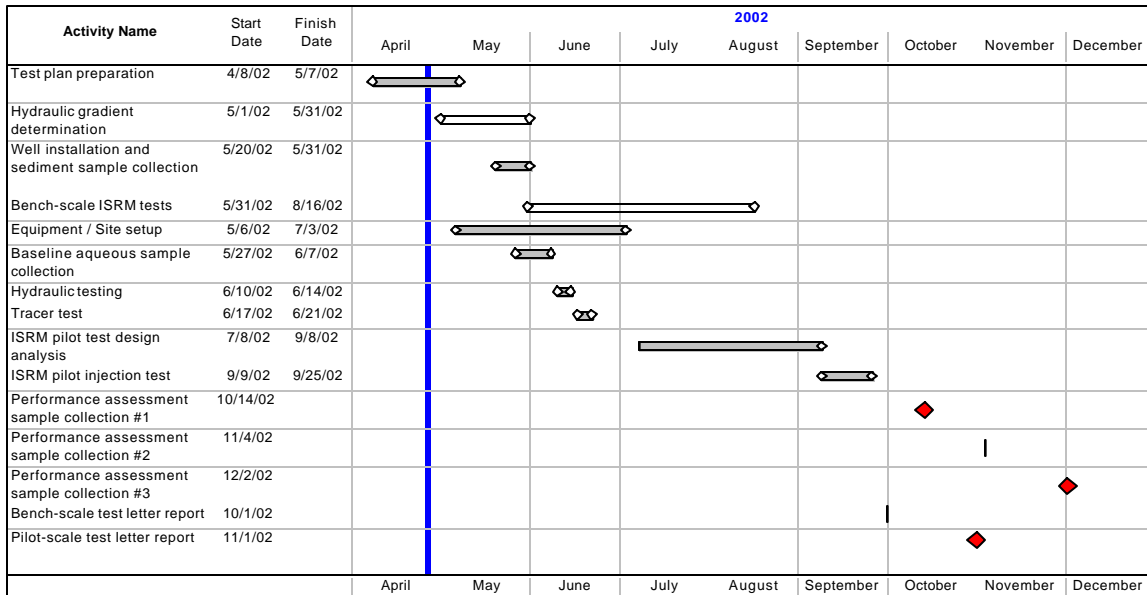
Upon completion of both the bench- and pilot-scale ISRM testing programs, PNNL will provide letter reports documenting the data collected, the available analysis results, and, if funding and time limitations allow, general guidance for the remedial design of the full-scale ISRM barrier at the FHC site.

6.0 Health and Safety Training requirements

All personnel working within site control zones must comply with the Occupational Safety and Health Administration (OSHA) regulations as defined in Title 29, *Code of Federal Regulations*, Part 1910 (29 CFR 1910). In addition to other requirements, these regulations require all on site personnel to receive a minimum of 40 hours training in health and safety for hazardous waste operations. In addition, the same personnel must be enrolled in a yearly medical surveillance program that includes a medical examination and work history review with special emphasis on symptoms related to the handling of hazardous substances and the fitness for duty. Personnel shall be certified as medically qualified to perform hazardous field activities or equivalent. Field personnel must successfully pass an annual respirator fit test, conducted in accordance with OSHA regulations, for the respiratory device(s) they will use. Supervisors must have received first aid/CPR training and attended the 8-hr supervisor's course. Additional relevant health and safety requirements specified in the FHC site health and safety plan developed by Weston will also be followed by PNNL project personnel.

7.0 Schedule

The following schedule is provided to facilitate coordination between PNNL and EPA/Weston field activities. Because PNNL field activities are dependent on milestones associated with well installation and development, sediment sample collection, and baseline aqueous sample collection, any slip in EPA's schedule for completing these activities will have an impact on subsequent ISRM remedial design testing activities.



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Appendix A
Sampling and Analysis Plan
In Situ Redox Manipulation Pilot Field Test

Frontier Hard Chrome
Vancouver, WA

April, 2002

1.0 SCOPE OF WORK

The scope of work encompassed in this Sampling and Analysis Plan (SAP) includes the collection and analysis of groundwater and aquifer sediment samples from the ISRM pilot field test at the Frontier Hard Chrome Site. Sample collection activities can be divided into three general categories including: 1) depth discrete sediment sample collection during installation of site monitoring wells, 2) baseline and post-injection performance assessment monitoring, and 3) operational monitoring (i.e., tracer and dithionite injection tests). Sample collection and analysis for each phase is discussed in the following sections.

2.0 SAMPLING OBJECTIVES

The primary objective of the sampling described in this SAP is to provide the characterization and monitoring data required to design and conduct a field-scale pilot demonstration of the In Situ Redox Manipulation (ISRM) technology. The following information will be obtained:

- Geologic characterization
 - lithologic descriptions
 - sediment physical properties (grain size distribution, porosity, bulk density)
 - geologic controls between A and B zone depth intervals
 - extent of upper silt unit
- Geochemical characterization
 - baseline groundwater chemistry
 - vertical distribution of hexavalent chromium contamination
 - ferrous/ferric iron [Fe(II)/Fe(III)] content
 - total ferric iron [Fe(III)] available for reduction
- Operational monitoring during field tests
 - tracer injection test
 - dithionite injection test
- Post-injection groundwater chemistry monitoring

3.0 GENERAL PROCEDURES

Field sampling will be conducted in accordance with the quality assurance section of this document (Section 5.0) and applicable project procedures. Each sample will be identified with a unique number to provide traceability of samples during collection, analysis, validation, and reporting. Samples will be either transported (under the appropriate preservation method) to on-site laboratory personnel responsible for analysis or shipped to the EPA Manchester laboratory for analysis. All sample handling will be documented on field data sheets or chain-of-custody forms, as required by Section 5.0 of the ISRM test plan.

4.0 SAMPLING STRATEGY

As previously stated, three general categories of sampling will occur during this ISRM remedial design testing program. The following sections provide a summary of the sampling requirements, and the frequency of sample collection, for each of the three types of samples that will be collected.

Analysis methods to be used on sediment and groundwater samples are discussed in Section 5. PNNL and/or EPA field sampling personnel will collect samples and deliver, or ship, samples to the appropriate laboratories for analysis.

4.1 Sediment Sample Collection

One of EPA's characterization objectives of this drilling campaign is to better define the depth extent of contamination and any geologic controls that may contribute to the differences in contaminant distribution observed between the A and B aquifer zones. This will be accomplished by collecting groundwater samples at various locations and depths using the geoprobe direct push sampler and analyzing the samples in the field for Cr(VI). These data will be used to determine the targeted depth interval for the ISRM treatment zone, and subsequently, the screen interval for the injection well and surrounding monitoring wells. Figure 3 of the ISRM test plan shows well locations within the pilot test site where sediment samples will be collected and Figure 1 shows the hydrogeologic conceptual model of the site.

During installation of the injection well and selected monitoring wells at the ISRM field test site, sediment samples will be collected by EPA and shipped to PNNL for laboratory analysis. For each A zone monitoring well indicated, a sediment sample will be collected from the top, middle, and bottom of the A zone depth interval. For each B zone monitoring well indicated, a sediment sample will be collected from the top, middle, and bottom of the A zone depth interval and a single sample will be collected from the B zone depth interval. In addition to samples collected at the ISRM pilot test site, sediment samples from the top, middle, and bottom of the A zone depth interval will also be collected from near the western and eastern extents of the anticipated full-scale barrier length.

Sediment samples will be collected using either a 2-in sampler with the geoprobe direct push method or using a nominal 4-in diameter split-spoon sampler in conjunction with a

standard drilling technique. In the case of the 4-in diameter split-spoon sampler, core sample will be collected within Lexan™ liner material pre-cut into 6-in long sections prior to loading them into the sampler. For the 2-in diameter geoprobe direct push sampler, 2 ft long acetate liners will be used. Sediment sampling requirements are contained in Table A.1. Sediment core samples collected for available iron and physical property analysis should be processed by EPA field personnel immediately following retrieval of the sampler, as follows:

- Remove sediment core samples from the sampler. In the case of the 4-in diameter Lexan™ lined samples, select one representative 6-in long section from the central portion of the split for processing. In the case of the 2-in diameter acetate lined samples, collect the full two foot length.
- Cap both ends of the Lexan™/acetate liner with vinyl end caps.
- Use Teflon™ or duct tape to seal the end caps. Write the date and time of sampling, the well number and depth, and the sampler's initials on the liner. Also show an arrow pointing in the up direction.

Because selected samples will also be analyzed to determine porosity and bulk density, samples must retain the sediment structure intact to the highest degree possible during sample collection and transport. To ensure that the sediment structure of the samples taken for these analyses remain intact, the Lexan™/acetate liners in which these samples are collected must be completely full of sediment. The sampled sediment will be sealed inside the liners with liner caps, and the caps taped in place. Samples do not require refrigeration during transport.

The split-spoon and direct push sampling equipment will initially be decontaminated by washing the sampler with a nonphosphate detergent and potable water, followed by rinsing with deionized water. The split-tube, head, shoe, spacer, core-catcher and liners will be assembled by personnel wearing new disposable rubber or plastic gloves. Once sediment samples have been analyzed, the samples will be returned to the site for disposal by EPA.

Table A1. Sediment Sampling Requirements.

| Parameter | Media/Matrix | Sampling Frequency ¹ | Volume/Container | Preservation |
|---|-----------------------|--|---|--------------|
| Physical Property Analysis: -grain size distribution -porosity -bulk density | Sediment ^a | Selected iron analysis core samples | 6-in long Lexan Liner Sleeve w/ End Caps **or** 2-ft long Acetate Liner Sleeve w/ End Caps | None |
| Iron Analysis | Sediment ^a | One sample from top, middle, and bottom of A zone (3 total); one additional sample from B zone in deep wells | 6-in long Lexan Liner Sleeve w/ End Caps **or** 2-ft long Acetate Liner Sleeve w/ End Caps | None |
| Lithologic Description | Sediment | Continuous by field inspection of cuttings | N/A | N/A |

^a Samples submitted to PNNL for analysis

4.2 Baseline and Performance Assessment Sampling

Baseline and post-injection performance assessment groundwater samples will be collected from the site by EPA and analyzed for hexavalent chromium and other constituents as listed in Table A.2. Performance of the test will be evaluated based on comparison of pre-test (baseline) conditions with geochemical conditions of the treatment zone following the ISRM pilot test.

Groundwater will be sampled using a portable 2-in-diameter variable speed submersible pump or comparable. The volume of water to be purged prior to sampling will be determined by field personnel at the time of sampling and will be based on stabilization of monitored field parameters. Collected groundwater samples will be handled in accordance with Section 5.0 of this SAP.

Non-dedicated sampling pumps will be decontaminated by placing it into a tub containing non-phosphate detergent and deionized water and then turning it on and allowing it to cycle the solution for a minimum of 5 minutes. Next the pump will be placed into a tub containing deionized water and cycled for another 5 minutes. The pump will then be placed in a third tub for a third and final deionized water rinse. Once groundwater samples have been analyzed, the samples will be disposed of by the sampling or laboratory personnel, in accordance with Section 4 of the ISRM test plan.

Table A2. Baseline and Performance Assessment Sampling Requirements.

| Parameter | Media/Matrix | Sampling Frequency | Volume/Container | Preservation |
|--|--------------------|---|-------------------------------------|---|
| Trace Metals: Na, Mg, K, Ca, Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Sb, Ba, Pb, U | Water ^a | 3 baseline and 3 post-injection sampling events per well | 25 ml plastic vial (acid washed) | Filtered, HNO ₃ to pH <2 |
| Anions: Cl ⁻ , Br ⁻ , SO ₄ ²⁻ , SO ₃ ²⁻ , PO ₄ ³⁻ , NO ₂ ⁻ , NO ₃ ⁻ | Water ^a | 3 baseline and 3 post-injection sampling events per well | 25 ml plastic vial | Zero headspace |
| Cr ⁶⁺ | Water | Same as Lab analyses above | Field Measurement | Filtered |
| pH | Water | Same as Lab analyses above | Field Measurement | None |
| Electrical conductivity | Water | Same as Lab analyses above | Field Measurement | None |
| Dissolved oxygen (DO) | Water | Same as Lab analyses above | Field Measurement | None |
| Oxidation- Reduction Potential (ORP) | Water | Same as Lab analyses above | Field Measurement | None |
| Temperature | Water | Same as Lab analyses above | Field Measurement | None |

^a Samples submitted to EPA Manchester Laboratory for analysis

4.3 Operational Monitoring

Operational monitoring will be performed by PNNL during all phases of the tracer injection and ISRM pilot injection tests to track operational performance and collect the required data to determine the extent and efficiency of the ISRM treatment zone emplacement. Dithionite concentration and other field parameters will be monitored, as listed in Table A.3.

Table A3. Operational Monitoring Requirements

| Parameter | Media/Matrix | Sampling Frequency | Volume/Container | Preservation |
|---|---------------------|--|-------------------------------------|--|
| Trace Metals: Na, Mg, K, Ca, Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Sb, Ba, Pb, U | Water ^a | Characterize trace metals in injection and withdrawal stream (~ 30 samples) | 25 ml plastic vial (acid washed) | Filtered, HNO ₃ to pH <2 |
| Wastewater: S, K, Na, Fe | Water ^a | Characterize high conc. analytes in injection and withdrawal stream (~ 30 samples) | 25 ml plastic vial (acid washed) | Filtered, HNO ₃ to pH <2 |
| Anions: Br ⁻ | Water ^a | Br ⁻ concentration verification samples from tracer test (~ 30 samples) | 25 ml plastic vial | Zero headspace; |
| Dithionite | Water | as required during injection monitoring | 25 ml plastic vial | None |
| pH | Water | as required during injection monitoring | Field Measurement | None |
| Electrical conductivity | Water | as required during injection monitoring | Field Measurement | None |
| Dissolved oxygen (DO) | Water | as required during injection monitoring | Field Measurement | None |
| Oxidation- Reduction Potential (ORP) | Water | as required during injection monitoring | Field Measurement | None |
| Temperature | Water | as required during injection monitoring | Field Measurement | None |

^a Samples submitted to EPA Manchester Laboratory for analysis

5.0 QUALITY ASSURANCE/QUALITY CONTROL

Sample collection and analysis for both sediment and aqueous samples will be performed according to the guidelines set forth in this section. Analytical methods to be used in both field and laboratory studies are summarized in Table A.4 for sediment samples and Table A.5 for aqueous samples. Since some of the methods used are to some extent non-standard in nature, additional details on those techniques are included in this section. While it is expected that all of the analyses discussed in Sections 5.1-5.2 shall be performed by the EPA Manchester Laboratory, data produced by these test methods are important to project objectives so additional discussion is provided. Other methods listed in the table are routine and require no further comment.

5.1 Filtered Metals

The list of elements shown in Table A.5 shall be subjected to ICP-MS analysis by the EPA Manchester Laboratory or equivalent contract laboratory. The method employed is EPA SW-846 Method 6020. Withdrawal samples will also be analyzed by inductively coupled plasma – optical emission spectroscopy (ICP-OES, EPA Method 6010) for the higher concentration analytes (S, K, Na, Fe). Samples shall be run in batches of up to 20. Each batch shall include at least one method blank, and matrix spike. It is expected that at least one multielement analysis shall be performed and reported for each sample submitted. Additional analyses may be performed as needed for QC purposes. Holding time requirements for metals analysis are very long and do not typically represent a technical limitation. Samples should be run in a timely manner to satisfy project objectives.

5.2 Anions

Common anions shall be measure by by the EPA Manchester Laboratory or equivalent contract laboratory using EPA Method 300.0 and ASTM method D4327. It is expected that at least one multianalyte analysis shall be performed and reported for each sample submitted. Additional analyses may be performed as needed for QC purposes.

Neither the EPA or ASTM methods cited have been validated for the analysis of sulfite. This species acts as reducing agent and is thus transient in the presence of oxygen. Samples shall be collected in a headspace free manner. If sulfite is observed in a chromatogram it shall be reported as an estimate based on the response factors obtained for sulfate.

Table A.4. Sediment Sample Analytical Requirements.

| Parameter | Analysis Method | Detection Limit | Typical Precision/Accuracy | QC Requirements |
|---|---|------------------------|-----------------------------------|------------------------|
| Grain Size Distribution | Sieve, ASTM or other Standard Method | Not applicable | Not applicable | None |
| Bulk Density/porosity | ASTM or other standard method | Not applicable | Not applicable | None |
| Available iron and reaction rate analysis | Dithionite Treatment (PNNL laboratory specific procedure) | Not applicable | Not applicable | None |

Table A.5. Aqueous Sample Analytical Requirements.

| Parameter | Analysis Method | Detection Limit | Typical Precision/Accuracy | QC Requirements |
|--|---------------------------------|----------------------------|----------------------------|--|
| Trace Metals: ^a Na, Mg, K, Ca, Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Sb, Ba, Pb, U | ICP-MS, (EPA-SW-846 6020) | 10 µg/L for trace elements | ±10% | Daily calibration; blanks and duplicates and matrix spikes at 10% level per batch of 20. |
| Wastewater: ^a S, K, Na, Fe | ICP-OES, (EPA-SW-846 6010) | 10 µg/L for sulfur species | ±10% | Daily calibration; blanks and duplicates and matrix spikes at 10% level per batch of 20. |
| Anions: ^a F ⁻ , Cl ⁻ , Br ⁻ , SO ₄ ²⁻ , SO ₃ ²⁻ , PO ₄ ³⁻ , NO ₂ ⁻ , NO ₃ ⁻ | Ion Chromatography (EPA-300.0) | 200 µg/L | ±15% | Daily calibration; blanks and duplicates at 10% level per batch of 20. |
| Dithionite | UV/Vis of HPLC | 0.0001 M | ±15% | For indication only |
| Cr ⁶⁺ | Hach DR-2000 w/ Accuvac Ampules | 0.007 mg/L | | Blanks |
| pH | pH electrode | Not applicable | ± 0.1 pH unit | User calibrate with pH buffer solutions |
| Electrical conductivity | Electrode | ± 1 µS/cm. | ±10% | User calibrate, blanks |
| Dissolved oxygen (DO) | Membrane electrode | ± 0.1 ppm | ±15% | User calibrate, blanks |
| Br ⁻ | Electrode | Not applicable | ±10% | For indication only |
| Oxidation-Reduction Potential (ORP) | Electrode | Not applicable | ±10% | For indication only |
| Temperature | Thermocouple | Not applicable | ± 1°C | Factory calibration |

^a Samples submitted to EPA Manchester Laboratory for analysis

