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TREATABILITY TEST PLAN FOR IN SITU REDOX MANIPULATION IN THE 100-HR-3 OPERABLE UNIT D-AREA

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ACRONYMS AND ABBREVIATIONS

ARAR	applicable or relevant and appropriate requirement(s)
ASTM	American Society for Testing and Materials
CERCLA	*Comprehensive Environmental Response, Compensation, and Liability Act of 1980*
DOE	U.S. Department of Energy
DQO	data quality objective
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
ERA	expedited response action
ERC	Environmental Restoration Contractor
ERDF	Environmental Restoration Disposal Facility
ETF	Effluent Treatment Facility
HEIS	Hanford Environmental Information System
ICP	inductively coupled plasma
ISRM	in situ redox manipulation
MS	mass spectrometer
NEPA	*National Environmental Policy Act of 1969*
PSDB	project-specific database
QA	quality assurance
QAPjP	Quality Assurance Project Plan
QMP	Quality Management Plan
RL	U.S. Department of Energy, Richland Operations Office
RWP	radiation work permit
SAP	Sampling and Analysis Plan
TBD	to be determined
Tri-Party Agreement	*Hanford Federal Facility Agreement and Consent Order*
WAC	*Washington Administrative Code* or waste acceptance criteria
WHC	Westinghouse Hanford Company

1.0 INTRODUCTION

The Hanford Site is located in southeastern Washington (Figure 1-1). It was established in 1943 to produce plutonium for nuclear weapons using reactors and chemical processing plants. The 100 Area of the Hanford Site is located along the Columbia River and includes nine deactivated U.S. Department of Energy (DOE) nuclear reactors used for plutonium production between 1943 and 1987. Operations at the Hanford Site are now focused on environmental restoration and waste management. In November 1989, the U.S. Environmental Protection Agency (EPA) designated the 100 Area of the Hanford Site a Superfund site and placed it on the National Priorities List because of soil and groundwater contamination that resulted from past operation of the nuclear facilities. To organize cleanup efforts under Superfund, contaminated areas at the nine deactivated reactors were subdivided into areas called "operable units."

The 100-HR-3 Operable Unit is located in the north-central part of the Hanford Site along a section of the Columbia River known as the "Hanford Reach." This operable unit includes the groundwater underlying the 100-D/DR and 100-H Reactor Areas and the 600 Area in between (Figure 1-2). The 100-D/DR Area is the site of two deactivated reactors: the 100-D Reactor, which operated from 1944 to 1967, and the 100-DR Reactor, which operated from 1950 to 1965. The 100-H Reactor operated from 1949 to 1965.

During reactor operations, hexavalent chromium or chromate, in the form of sodium dichromate ($Na_2Cr_2O_7$), was used as an anticorrosion agent in the reactor cooling water. Large volumes of reactor coolant water, containing sodium dichromate and short-lived radionuclides, were discharged to retention basins for ultimate disposal in the Columbia River through outfall pipelines. Liquid wastes from other reactor operations (decontamination, water treatment, etc.) also contained significant quantities of hexavalent chromium. These wastes were discharged to the soil column at cribs, trenches, and french drains, or leaked from storage facilities. Contaminant plumes in groundwater resulted from these former waste disposal practices. Groundwater contaminated with hexavalent chromium is present beneath the 100-D/DR and 100-H Reactor Area and is flowing toward and entering into the Columbia River from the natural water-table gradient (see Figure 1-3).

In addition to the reactor areas, high concentrations (~ 1,000 µg/L) of hexavalent chromium have recently been detected in the groundwater in the 100-HR-3 Operable Unit is along the western edge of the 100-D/DR Area at well 199-D4-1. This is the location of the proposed Treatability Test described in this plan (see Figure 1-4). Well 199-D4-1 was drilled following a characterization program that detected hexavalent chromium concentrations in excess of 630 µg/L in the pore waters of the Columbia River substrate along the 100-D/DR Area (Connelly, 1997) as shown in Figure 1-3. The elevated hexavalent chromium concentrations detected in the pore waters of the river substrate pose a potential risk to aquatic organisms in the Columbia River. The 199-D4-1 well (which was drilled approximately 152 m (500 ft) inland from the highest concentrations measured in the river substrate pore water) helped identify groundwater as the source of the hexavalent chromium in the Columbia River substrate porewater (Connelly, 1997). The areal extent of the plume and the original source of this groundwater plume has not been adequately defined due to the limited number of monitoring wells in the area.

In Situ Redox Manipulation (ISRM) technology involves creating a permeable subsurface treatment zone to reduce mobile chromate in groundwater to an insoluble form. An unconfined aquifer is usually an oxidizing environment; therefore, most of the contaminants that are mobile in the aquifer are those that are mobile under oxidizing conditions. If the redox potential of the aquifer can be

made reducing, then a variety of contaminants could be treated. A successful ISRM proof-of-principle experiment was conducted in the 100-H Area in 1995 (Fruchter et al, 1996) that demonstrated the ability to alter the redox potential of the unconfined aquifer at the Hanford Site and to remove chromate from the groundwater.

The goal of the ISRM treatability test is to create a subsurface permeable treatment zone for remediation of chromate contamination in aquifers. This permeable treatment zone is created by reducing the ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}) within the aquifer. This is accomplished by injecting sodium dithionite into the aquifer and withdrawing unreacted reagent and reaction products. The sodium dithionite serves as a reducing agent for iron, changing ferric iron to ferrous iron within the unconfined aquifer sediments. Chromate ($Cr_2O_7^{2-}$), which is anionic in nature and soluble in groundwater, contains hexavalent chromium, Cr^{6+}. The altered subsurface environment containing the reduced iron will then act upon the Cr^{6+} species, reducing it to Cr^{3+}, which will then precipitate from the groundwater as $Cr(OH)_3$, thereby immobilizing the chromium.

1.1 PURPOSE AND SCOPE

The *Proposed Plan for Interim Remedial Measure at the 100-HR-3 Operable Unit* (DOE-RL1995b) identified the preferred alternative for an interim remedial measure at the 100-HR-3 Operable Unit. The preferred alternative is to pump contaminated groundwater from the 100-HR-3 Operable Unit, treat it by ion exchange, and dispose of treated groundwater by using upgradient injection wells to return it to the aquifer. The proposed plan also considered the possibility that alternative technologies could immobilize hexavalent chromium in the aquifer without pumping and treating. One of those technologies, ISRM, would immobilize hexavalent chromium by changing the soil and water chemistry in the aquifer and reducing the chromium to the less toxic and less mobile trivalent form. The ISRM technology offers promise of preventing the movement of hexavalent chromium to sensitive ecological receptors, without creating the secondary waste associated with surface treatment technologies, while reducing the need for long-term operation and maintenance compared to pump and treat. ISRM technology could result in substantial cost savings as compared to pump-and-treat methods of groundwater plume remediation.

In general, the ISRM technology changes the redox potential of the groundwater through subsurface injection of chemical reducing agents. The chemical agents reduce the naturally occurring ferric iron found within the clay minerals of the aquifer sediments. Reagent and reaction products can be removed (withdrawn) from the subsurface after the aquifer sediments are reduced. Redox-sensitive contaminants migrating through this reduced zone (treatment zone) are in turn reduced and immobilized or degraded. This treatability test will demonstrate the ISRM technology on a pilot scale in the 100-D Area. Reduction of ferric iron will be accomplished by injecting and withdrawing aqueous sodium dithionite into the aquifer. Hexavalent chromium in the groundwater moving through this zone will be reduced to the less soluble and less toxic trivalent form of chromium.

Pacific Northwest National Laboratory (PNNL), the developer of the ISRM technology, has conducted experiments to test the viability of the ISRM technology (see Fruchter et al., 1994, 1995, and 1996). These experiments have included a range of tests from bench-scale to field-scale testing. The ISRM Project began in fiscal year (FY) 1992 through DOE's Office of Health and Environmental Research - Subsurface Science Program. As part of this ISRM project,

laboratory proof-of-principle abiotic and biotic studies, conceptual design reports, and preliminary planning documents were prepared (Fruchter et al. 1995). The potential for a remediation technology based on in situ manipulation of subsurface redox conditions has been established through theory and proof-of-principle laboratory experiments. However, attempts to control redox potential in an aquifer must overcome various scale-up complications arising from the interaction between contaminants, reducing agents, groundwater, and the natural variability of the subsurface. In FY 1994, a site at 100-H Area was selected for field-scale experiments of the ISRM technology. The laboratory and design studies as well as the FY 1994 and 1995 field tests were funded through DOE's Office of Technology Development's In Situ Remediation Integrated Program. Results of these experiments will be used to design this full-scale field demonstration.

The specific objective of this demonstration project is to gather information pertinent to the full-scale implementation of the technology. In order to be accepted as a method of remediation under the *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* (CERCLA), a technology must be evaluated on the basis of nine criteria of interest, as discussed below.

The nine criteria the EPA uses to identify its preferred alternative for a given site include two "threshold" criteria, five "balancing" criteria, and two "modifying" criteria. To be selected, an alternative must first meet the threshold criteria. The balancing criteria are used for comparing alternatives and selecting a preferred alternative. After public comment, the EPA may alter its preference on the basis of two modifying criteria (which will not be addressed by this treatability test).

Threshold Criteria:

1. **Overall Protection of Human Health and the Environment** - How well does the alternative protect human health and the environment, both during and after construction?

2. **Compliance with Applicable or Relevant and Appropriate Requirements** - Does the alternative meet all federal and state applicable or relevant and appropriate requirements (ARARs)?

Balancing Criteria:

3. **Long-Term Effectiveness and Permanence** - How well does the alternative protect human health and the environment after completion of cleanup? What, if any, risks will remain at the site?

4. **Reduction of Toxicity, Mobility, or Volume Through Treatment** - Does the alternative effectively treat the contamination to significantly reduce the toxicity, mobility, and volume of the hazardous substances?

5. **Short-Term Effectiveness** - Are there potential adverse effects to either human health or the environment during construction or implementation of the alternative? How quickly does the alternative reach the cleanup goals?

6. **Implementability** - Is the alternative both technically and administratively feasible? Has the technology been used successfully on other similar sites?

7. **Cost** - What are the estimated costs of the alternative?

Modifying Criteria:

8. **State Acceptance** - What are the state's comments or concerns about the alternatives considered and about EPA's preferred alternative? Does the state support or oppose the preferred alternative?

9. **Community Acceptance** - What are the community's comments or concerns about the preferred alternative? Does the community generally support or oppose the preferred alternative?

This treatability test will provide data that pertain to the first seven criteria.

1.2 TEST SITE SELECTION

Site selection for implementing the ISRM treatability study involved data evaluation of areas where chromate (Cr^{6+}) is present in the unconfined aquifer. Chromate concentration was the foremost consideration for locating the test site. Available groundwater data did not specifically identify chromate concentrations, but filtered, total chromium concentrations. Since hexavalent chromium is much more soluble in water than the trivalent form, hexavalent chromium is assumed to predominate.

Sodium dichromate was used during reactor operations as an anticorrosion agent and also for decontamination activities. As a result of these operations, chromium has been detected in groundwater at the 100-D, 100-F, 100-H, 100-K, and 100-N areas, where these activities took place. Recent data indicates that chromium at 100-D exists in concentrations >1,000 ppb (see Figure 1-3), specifically in the 105-D Reactor area and on the western side of D Area in a well drilled in October 1996 (199-D4-1).

Based on the chromium concentration in the aquifer recently detected in Well 199-D4-1 and its proximity to the Columbia River (0.15 km [~ 500 ft]), this area was chosen as the principal location for implementing the ISRM treatability study (see Figure 1-4). However, additional subsurface data from this area are needed to determine the amount of reagent required and the orientation and depth of the barrier relative to the chromate plume. Additional subsurface data requirements include:

- Sufficient ferric iron present in aquifer sediments
- Chromate concentration in areas around Well 199-D4-1
- Lateral extension of confining unit
- Hydraulic Conductivity of aquifer
- Hydraulic gradient
- Physical properties of aquifer sediment (porosity, grain size distribution)

1.3 SITE DESCRIPTION

The 100-HR-3 Groundwater Operable Unit is located in the 100 Area of the Hanford Site and comprises the 100-H Area, the 100-D Area, and the 600 Area between the two (Figure 1-2). The

100-D Area is located in the 100-HR-3 Groundwater Operable Unit and consists of a site of past reactor operations, 105-D and 105-DR. Because of the nature and extent of past practices, chromium contamination is present in groundwater in concentrations exceeding regulatory limits and has been determined to be a contaminant of potential concern (DOE-RL 1993). The 100-D Area is a focal point for groundwater remediation.

1.3.1 Geology

Geologic information for the site is based on the borehole log from well 199-D4-1. In this 32 m (105 ft) deep borehole, the Hanford formation is present from 0-17m (0-55 ft); a coarse-grained unit of the Ringold Formation is present from 17 m-30 m (55-98 ft); and a fine-grained unit of the Ringold Formation is present from 30 m - 32 m (98-105 ft) as shown in Figure 1-5. Hanford formation sediments encountered consist of 0.6 m - 3.4 m (2-11 ft thick) interbedded sand and sandy gravel layers. Coarse-grained Ringold Formation deposits underlie the Hanford formation; these deposits consist of sandy gravels to sandy silty gravels. Based on previous work in the 100-HR-3 Operable Unit by Lindsey and Jaeger (1993), these gravels probably represent Unit E of the Ringold formation as defined by Lindsey (1991, 1995). Underlying the Unit E gravels is a pale brown silty clay. This silty clay probably represents overbank-paleosol deposits; these overbank-paleosol deposits stratigraphically overlie the Ringold lower mud unit within the 100-D Area (Lindsey and Jaeger 1993).

1.3.2 Hydrogeology of the Unconfined Aquifer

The unconfined aquifer is approximately 4.9 m (16 ft) thick beneath the site and is contained within the sandy gravels and silty sandy gravels of the Ringold Formation, Unit E. A overbank-paleosol facies of the Ringold Formation, represented by a silty clay, forms the base of the upper unconfined aquifer. Limited hydrologic information is available for well 199-D4-1. This information is limited to a specific capacity measurement of 50 L/Min/m obtained during well development activities (Johnson et al. 1996). A summary table of hydrogeologic information for well 199-D4-1 is shown in Table 1-1.

The hydraulic gradient (direction and magnitude) in the area of well 199-D4-1 has not been characterized due to the limited number of wells in the area. Given the proximity of the site to the Columbia River, the groundwater flow is assumed to be predominantly toward the river (toward the northwest). During times of high river stage, the groundwater flow direction may reverse 180 degrees (toward the southeast), pointing away from the river. These assumptions are based on a detailed analysis of well networks located a similar distance from the river at the nearby 100-N Area.

1.3.3 Groundwater Contamination

A table of groundwater data for well 199-D4-1 is shown in Table 1-2. Elevated constituents in this table consist of chromium (908 µg/L, filtered; 957 µg/L, unfiltered) and nitrate (58.4 mg/L). These values for chromium and nitrate are above the maximum contaminant levels (MCL) for these constituents (50 µg/L and 45 mg/L, respectively).

A plume map of chromium concentrations in the 100-D Area is shown in Figure 1-3. The plume is not well defined in the area of Well 199-D4-1. Potential sources for the chromate contamination in the western portion of the D-Area include leaks from the Sodium Dichromate Transfer Station

and the associated french drain, the Process Sewer (100-DR process sewer) used to discharge wastes from the 183-DR and 190-DR water treatment facilities (sodium dichromate preparation for reactor coolant water), and/or the four 3.75 million gallon tanks (190-DR) used to store sodium dichromate solutions prior to use for reactor cooling. The 190-DR tanks have been removed and the area was subsequently used for a pit burial ground (126-DR-1). Use of this burial ground was discontinued due to potential chromate contamination of the soil and uncontrolled dumping (Carpenter, 1993, p. 5-18). A description of all these facilities can be found in Carpenter, 1993.

During reactor operations, large quantities of cooling water from the reactors was discharged into retention basins to provide for a "cooling off" period prior to discharge into the river. The groundwater flow direction in the area was altered by groundwater mounding created from leakage from the retention basins. An analysis of the historical groundwater flow directions in the D-Area was conducted by Connelly (1997). This analysis showed that the extensive groundwater mounding in the northeast portion of the D-Area added a western component to the groundwater flow directions in the western side of the D-Area during reactor operations. Thus, potential sources of the chromate plume detected at 199-D4-1 could be located further to the east than that which would be inferred from the current (i.e., post-reactor operations) water table and could include any or all of the potential sources already discussed.

1.4 PREVIOUS TREATABILITY STUDIES

A previous treatability study conducted at the 100-HR-3 Operable Unit was the pilot-scale pump-and-treat system. Initially bench tested, this ion-exchange type system was implemented at the 100-D Reactor area in August 1994 for treating chromate-contaminated groundwater in response to a Tri-Party Agreement milestone (Ecology et al. 1990). The test was conducted in two phases: phase one, operation of the pump-and-treat system 8 hr/day and 5 days/week; and phase two, operation of the pump-and-treat system 24 hr/day and 7 days/week.

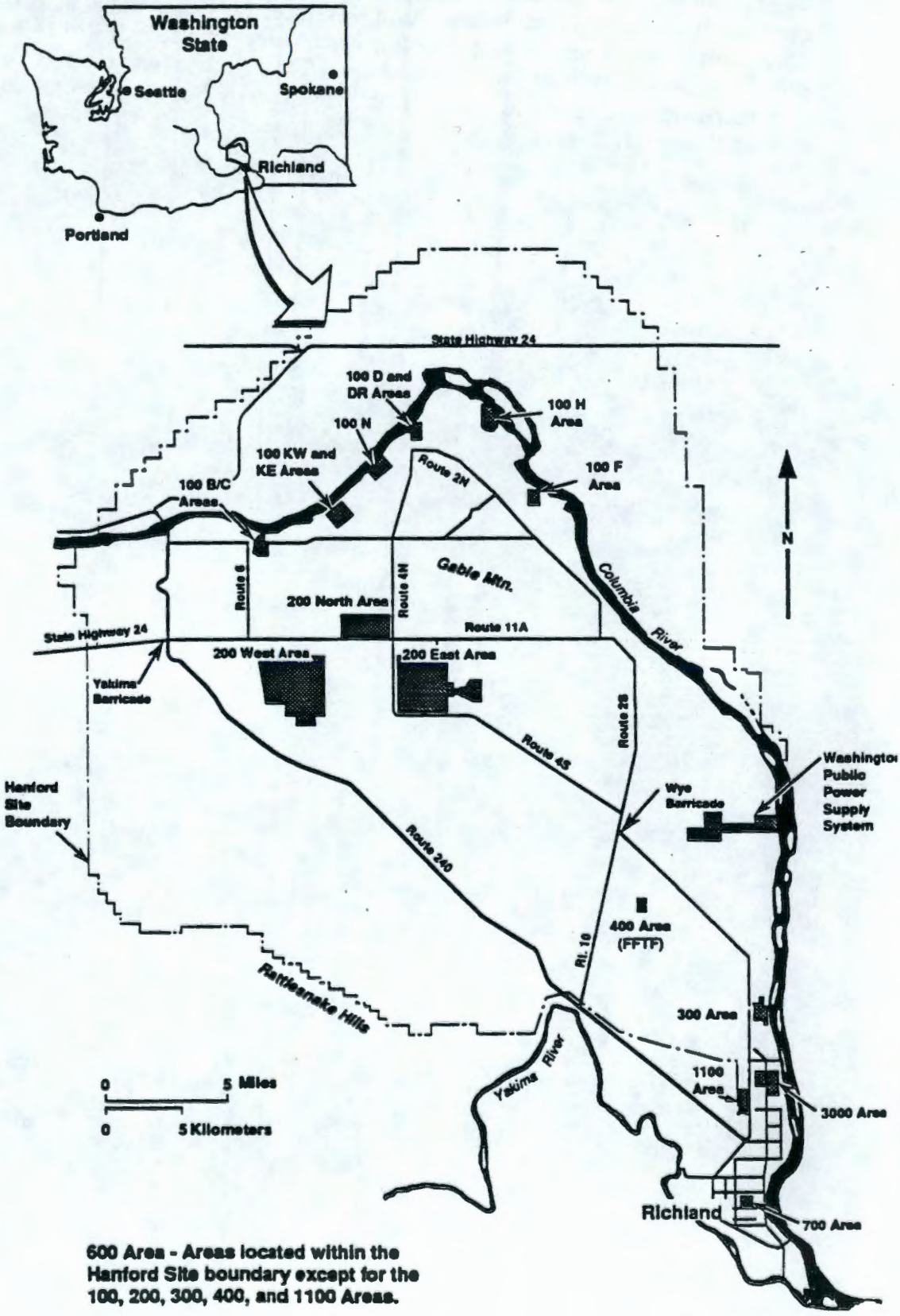
The objective of the pilot-scale demonstration was to determine the feasibility of the pump-and-treat system in treating chromium-contaminated groundwater. The test location was chosen at 100-D because high concentrations of chromium are present in the groundwater. The pump-and-treat extraction and injection network was set up using existing wells located in the 100-D/DR Reactor area. These existing wells were constructed as monitoring wells and were not specifically constructed for this pilot-scale study. Wells 199-D5-14, 199-D5-15, and 199-D5-16 were selected for extraction wells because of their location within the downgradient side of the chromium plume. Wells 199-D5-18 and 199-D5-19 were selected as injection wells within the upgradient side of the chromium plume.

The primary objective of the pump-and-treat pilot-scale treatability test was to determine the feasibility of treating chromium-contaminated groundwater to <50 ppb. The drinking water standard for chromate is 50 ppb as determined by the *Washington Administrative Code* (WAC), Chapter 173-303-645. The chromium-contaminated groundwater is extracted and treated ex situ using a strong base resin. Once the groundwater is treated ex situ, it is injected back into the aquifer via wells 199-D5-18 and 199-D5-19, upgradient of the chromium plume.

The pump-and-treat system was initially designed to operate manually on a 5-days/week, 8-hr/day basis. It was later reconfigured to operate automatically on a continuous basis. Phase I (manual) operations began on August 26, 1994, and lasted until November 14, 1994. Phase II (automated) operations were initiated March 21, 1995, and were ended in the summer of 1996.

The system was able to accomplish its primary objective, which was to achieve an effluent concentration of <50 ppb chromate. As of November 1, 1995, the total mass of hexavalent chromium removed was 29.9 kg (65.8 lb), which is approximately 9% to 14% of the total mass of chromate that was estimated to be in the plume. The objectives and results of the Phase I and II operations are summarized in *The Pilot-Scale Treatability Test Summary for the 100-HR-3 Operable Unit* (DOE-RL 1995c).

Figure 1-1. Hanford Area Site Map



600 Area - Areas located within the Hanford Site boundary except for the 100, 200, 300, 400, and 1100 Areas.

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Figure 1-2. 100-HR-3 Operable Unit.

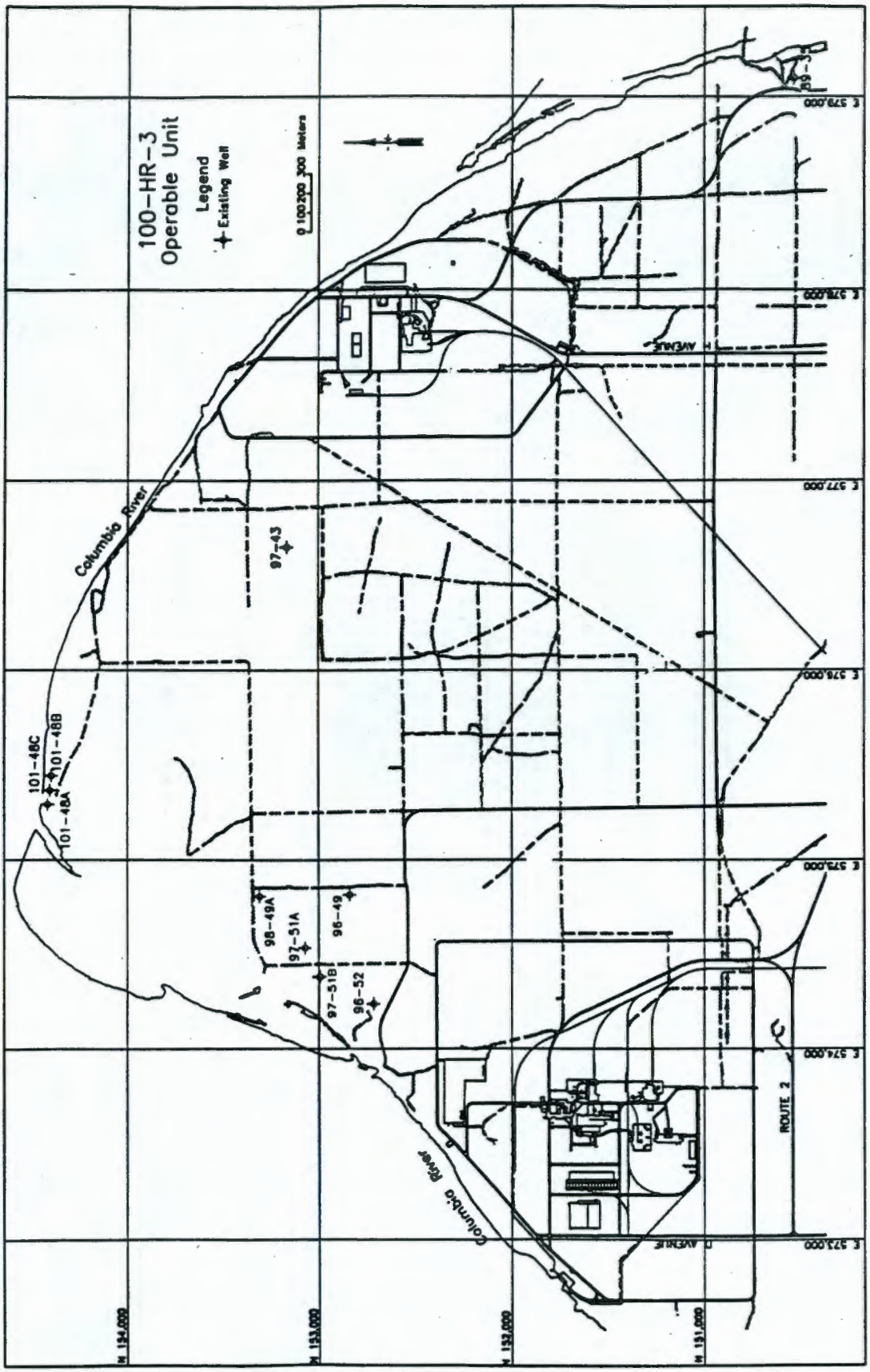

Figure 1-3. 100-D Area Chromium (VI) Groundwater Contaminant Plume.

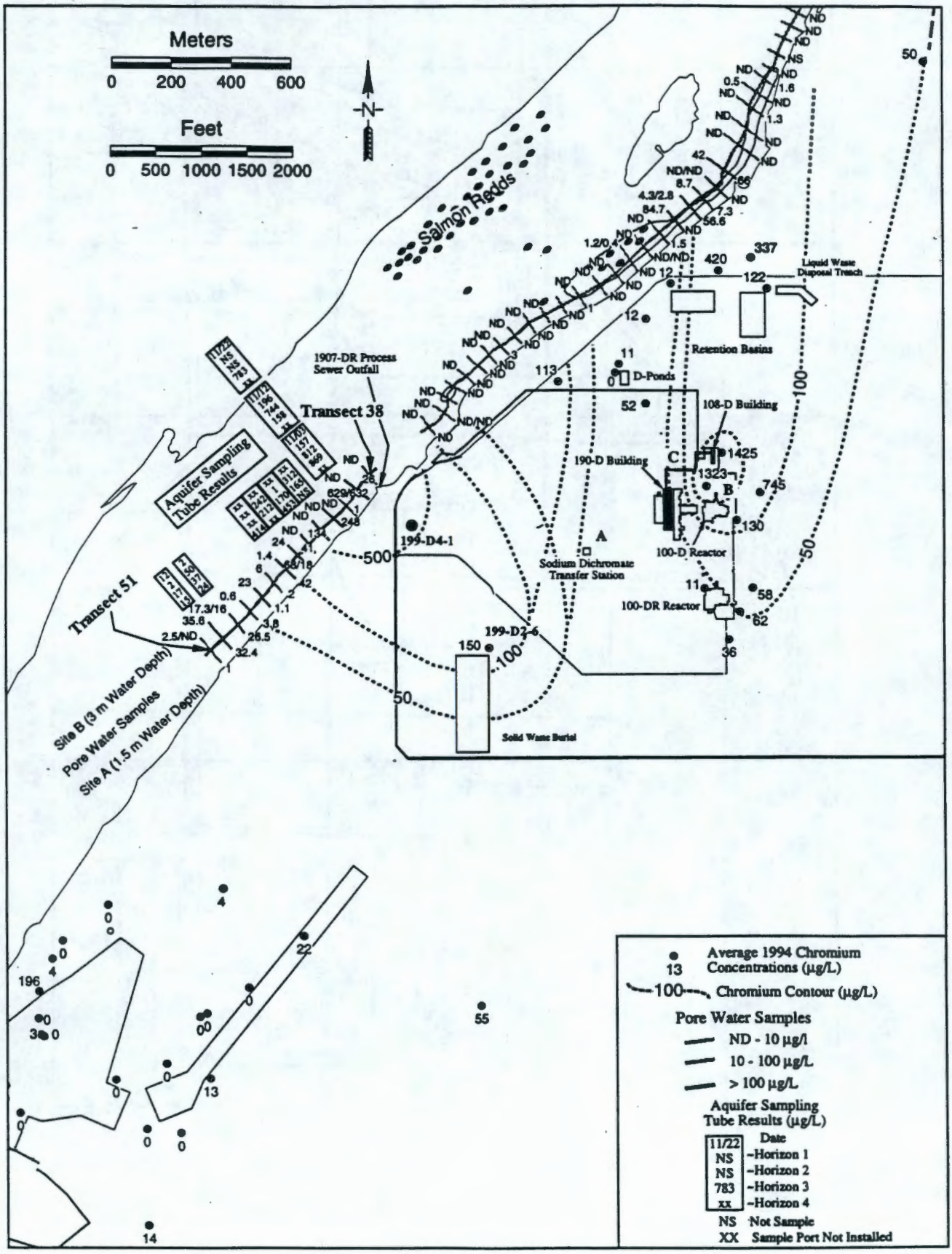

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Figure 1-4. Location of the Proposed ISRM Treatability Study at 100-D/DR Area.

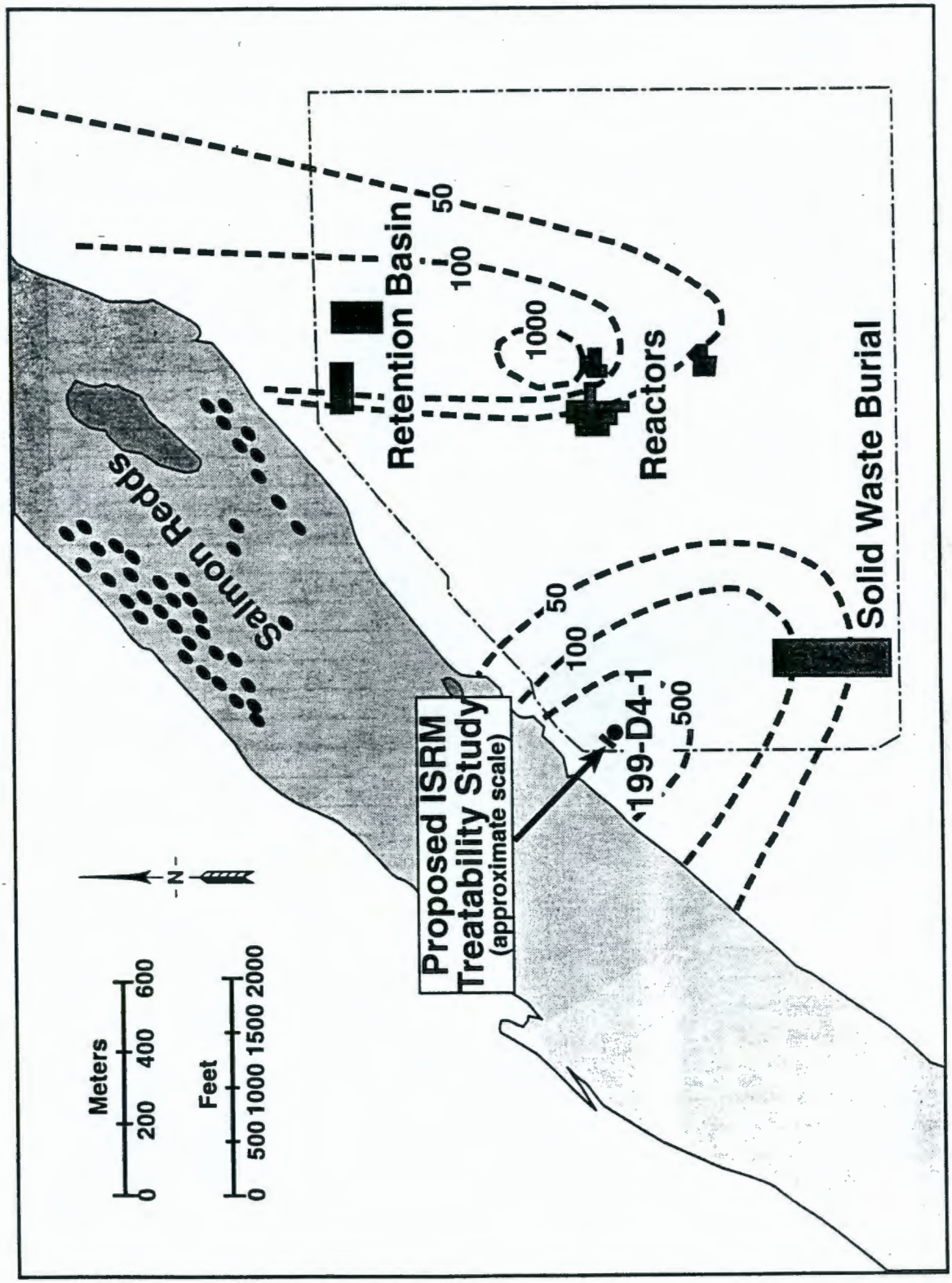

Figure 1-5. Geologic log of well 199-D4-1.

WELL SUMMARY SHEET

Boring or Well No. 199-D4-1

Sheet 1 of 1

Location ~2 mile west of D Reactor

Project 100-HR-3 IRM

Reviewed By EDWARD C. RAFOC / Edward C. Rafoc 10/31/96

Prepared by [illegible] / L.D. Walker

CONSTRUCTION DATA: Description	Depth in Feet	GEOLOGIC/HYDROLOGIC DATA: Lithologic Description
		0-2': Sandy Gravel (sG)
		2'-5': Silty Sand (mS)
Cement Grout: 0-64.8'	10	5'-10': Sandy Gravel (sG)
		10'-13': Sand (S)
	20	13'-23': Sandy Gravel (sG)
		23'-27': Sand (S)
6" stainless steel casing:	30	27'-30': Sandy Gravel (sG)
+.60' → 74.65'		30'-41': Sand (S)
	40	41'-55': Sandy Gravel (sG)
		Hanford-Ringold contact: 55'
10-20 silica sand: 64.8'-67.4'	50	
6-12 silica sand: 67.4'-70.2'		55'-70': Sandy Gravel (sG)
4-10 silica sand: 70.2'-104.9'	60	
	70	70'-80': Silty Sandy Gravel (msG)
6" stainless steel wire wrap		
0.060 slot screen:	80	80'-95': Sandy Gravel (sG)
74.65'-94.67'		
	90	95'-98': Silty Sandy Gravel (msG)
Bottom of 6" stainless steel		
tailpipe: 97.72'	100	98'-105': Silty Clay (M)
	110	TD = 105'
		Water Level = 81.90' (10-30-96)
Depths are measured		
from ground surface		

Diagram / Graphic Log

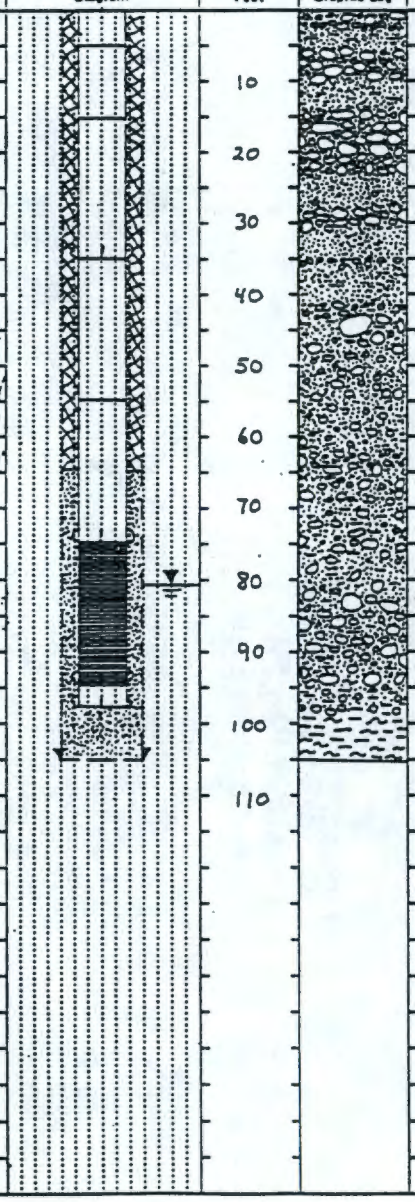

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Table 1-1. Summary of available hydrogeologic information for well 199-D4-1.

PARAMETER	VALUE
Depth to Water Table	25.0 m (81.9 ft)
Depth to top of Ringold Formation, Unit E (from ground surface)	17 m (55 ft)
Depth to top of Ringold, overbank-paleosol facies (from ground surface)	30 m (98 ft)
Saturated thickness of aquifer	4.9 m (16 ft)
Dominant aquifer lithology	Sandy Gravel to Silty Sandy Gravel
Lithology of aquifer lower boundary (Ringold fine grained facies)	Silty Clay
Surface Elevation	143.13 m (469.59 ft)
Specific Capacity	50 L/Min/m

Table 1-2. Groundwater Chemistry for Well 199-D4-1.

WELL NAME	SAMP DATE TIME	CON LONG NAME	SAMP FILTERED	VALUE RPTD	QUALIFIER	ANAL UNITS RPTD	COUNTING ERROR
199-D4-1	10/31/96 11:52	Aluminum	N	238		ug/L	
199-D4-1	10/31/96 11:52	Aluminum	Y	58.5	U	ug/L	
199-D4-1	10/31/96 11:52	Antimony	N	32.5	B	ug/L	
199-D4-1	10/31/96 11:52	Antimony	Y	41.8	B	ug/L	
199-D4-1	10/31/96 11:52	Barium	N	75.8	B	ug/L	
199-D4-1	10/31/96 11:52	Barium	Y	73.4	B	ug/L	
199-D4-1	10/31/96 11:52	Beryllium	N	0.4	U	ug/L	
199-D4-1	10/31/96 11:52	Beryllium	Y	0.4	U	ug/L	
199-D4-1	10/31/96 11:52	Cadmium	N	3	U	ug/L	
199-D4-1	10/31/96 11:52	Cadmium	Y	3	U	ug/L	
199-D4-1	10/31/96 11:52	Calcium	N	81200		ug/L	
199-D4-1	10/31/96 11:52	Calcium	Y	77700		ug/L	
199-D4-1	10/31/96 11:52	Chloride	N	26.7		mg/L	
199-D4-1	10/31/96 11:52	Chromium	Y	908		ug/L	
199-D4-1	10/31/96 11:52	Chromium	N	957		ug/L	
199-D4-1	10/31/96 11:52	Cobalt	Y	3	U	ug/L	
199-D4-1	10/31/96 11:52	Cobalt	N	3	U	ug/L	
199-D4-1	10/31/96 11:52	Copper	Y	13.9	B	ug/L	
199-D4-1	10/31/96 11:52	Copper	N	14.4	B	ug/L	
199-D4-1	10/31/96 11:52	Fluoride	N	0.14		mg/L	
199-D4-1	10/31/96 11:52	Gross alpha	N	0.994	U	pCi/L	0.801
199-D4-1	10/31/96 11:52	Gross beta	N	7.6		pCi/L	1.89
199-D4-1	10/31/96 11:52	Iron	Y	13.7	BE	ug/L	
199-D4-1	10/31/96 11:52	Iron	N	329	E	ug/L	
199-D4-1	10/31/96 11:52	Magnesium	N	18200		ug/L	
199-D4-1	10/31/96 11:52	Magnesium	Y	17400		ug/L	
199-D4-1	10/31/96 11:52	Manganese	Y	6.8	B	ug/L	
199-D4-1	10/31/96 11:52	Manganese	N	21.5		ug/L	
199-D4-1	10/31/96 11:52	Nickel	Y	13.4	U	ug/L	
199-D4-1	10/31/96 11:52	Nickel	N	13.4	U	ug/L	
199-D4-1	10/31/96 11:52	Nitrate	N	58.4		mg/L	
199-D4-1	10/31/96 11:52	Potassium	Y	5160		ug/L	
199-D4-1	10/31/96 11:52	Potassium	N	3430	B	ug/L	
199-D4-1	10/31/96 11:52	Silver	Y	6.6	U	ug/L	
199-D4-1	10/31/96 11:52	Silver	N	6.6	U	ug/L	
199-D4-1	10/31/96 11:52	Sodium	Y	8820		ug/L	
199-D4-1	10/31/96 11:52	Sodium	N	9270		ug/L	
199-D4-1	10/31/96 11:52	Sulfate	N	109		mg/L	
199-D4-1	10/31/96 11:52	Tritium	N	438		pCi/L	158
199-D4-1	10/31/96 11:52	Vanadium	Y	14.2	B	ug/L	
199-D4-1	10/31/96 11:52	Vanadium	N	15.1	B	ug/L	
199-D4-1	10/31/96 11:52	Zinc	Y	50.4		ug/L	
199-D4-1	10/31/96 11:52	Zinc	N	49.1		ug/L	

2.0 TREATMENT TECHNOLOGY DESCRIPTION

The ISRM approach is to be implemented as an innovative treatability test to inhibit the spread of redox-sensitive contaminants by reducing the potential for contaminant migration in the aquifer. A multi-scale approach, including bench-scale and field-scale experiments, was used during development of the ISRM technology. The intent of this ISRM treatability study involves constructing a permeable subsurface treatment zone to determine feasibility and compare costs with existing remediation technologies.

2.1 TREATMENT CHEMISTRY

The redox altering reagent to be injected is sodium dithionite ($Na_2S_2O_4$). The dithionite (also commonly known as hydrosulfite) ion ($S_2O_4^{2-}$) in the injection solution is a strong reductant, particularly in strongly basic solutions (Amonette et al. 1994). This ion dissociates:

$$S_2O_4^{2-} \Leftrightarrow 2\ SO_2^{\bullet -}$$

into sulfoxyl radicals ($SO_2^{\bullet -}$), which are strong and highly reactive reductants. According to Amonette et al. (1994), reduction reactions with the dithionite ion typically involve two steps:

1. Dissociation of the ion to form the two $SO_2^{\bullet -}$ radicals

2. Reaction of these radicals with the oxidized species [e.g., Fe(III) contained in layered silicate and oxide minerals] yields a reduced species [e.g., Fe(II) contained in layered silicate minerals or as a soluble species (Fe^{2+})] and sulfite (SO_3^{2-}) or bisulfite ($HS0_3^-$).

Because sulfoxyl radicals ($SO_2^{\bullet -}$) are highly reactive, the dissociation of the dithionite ion ($S_2O_4^{2-}$) is the slow or rate-limiting step in most reactions.

2.1.1 Reduction Reactions

The desired reduction reaction with the dithionite ion takes place very quickly; half-life of the reaction based on laboratory data is on the order of 1 to 3 hr with sediments typically found at Hanford (both Ringold and Hanford formation sediments). The available ferric iron [Fe(III)] in the sediments of the aquifer is reduced to ferrous iron [Fe(II)] by the following reaction:

$$SO_2^{\bullet -} + Fe(III) + H_2O \Leftrightarrow SO_3^{2-} + Fe(II) + 2\ H^+.$$

The most available/accessible forms of iron in the subsurface sediments occur in those mineral phases (i.e., iron oxyhydroxides and iron-bearing layer silicates) with the highest specific surface areas (Amonette et al. 1994). It is desirable for the reduced iron species [i.e., Fe(II)] to remain in place, so the clay- and silt-sized iron-bearing layer silicates are being targeted because the iron in this mineral phase is retained in the mineral structure regardless of its oxidation state (Stucki 1988, Scott and Amonette 1988). In contrast, the iron oxyhydroxide mineral phase dissolves when its

iron is reduced unless there is sufficient carbonate for siderite ($FeCO_3$) to precipitate (Amonette et al. 1994).

Samples of Ringold Formation sediments taken from well 199-D5-19 at depths ranging from 22.4 m to 29 m (73.5 to 95 ft) indicate that ferric iron averages about 0.88% based on the maximum assumption of 19 wt% clay.

2.1.2 Disproportionation Reaction

The dithionite ion is not stable in acidic or neutral pH aqueous solutions for long periods. In addition to the reduction reactions discussed above, the dithionite ion undergoes a disproportionation reaction that yields thiosulfate, $S_2O_3^{2-}$, and bisulfite, HSO_3^-:

$$2\ S_2O_4^{2-} + H_2O \Leftrightarrow 2\ HSO_3^- + S_2O_3^{2-}.$$

This disproportionation reaction rate is slower than the reduction reaction rates discussed above and depends on the nature of the mineral surfaces encountered. Estimates of the reaction half-life based on laboratory experiments are on the order of 10 to 20 hr. The byproducts of both the reduction and disproportionation reactions (i.e., sulfites, bisulfites, and thiosulfates) all eventually oxidize (at much slower rates) to yield sulfate.

2.1.3 Composition of Reagent Solution to be Injected

The reagent solution to be injected is composed of sodium dithionite with a potassium carbonate/bicarbonate buffer. The buffer is used to maintain a relatively high pH because it enhances dithionite stability. The composition of the injected reagent for the experiment is typically 0.1 M sodium dithionite ($Na_2S_2O_4$), 0.4 M potassium carbonate (K_2CO_3), and 0.04 M potassium bicarbonate ($KHCO_3$). The pH of the injection solution is ~11 with a density of 1.06 g/cm^3.

2.1.4 Chromium Reduction, Groundwater Deoxygenation, and Metals Mobilization

Once a redox zone has been emplaced, the reduced iron in the sediments treated with dithionite will act to reduce the mobile Cr(VI) phase of chromium (CrO_4^{2-}) in migrating groundwater at a chromium-contaminated site. The reduction reaction converts the mobile phase to a precipitated Cr(III) phase [$Cr(OH)_3$] as follows:

$$3\ Fe(II) + CrO_4^{2-} + 5\ H^+ \Leftrightarrow Cr(OH)_{3\,(s)} + 3\ Fe(III) + H_2O\ .$$

The reduced sediments at the experimental site will remove any dissolved oxygen in the migrating groundwater by the following reaction:

$$4\ Fe(II) + O_2 + 4\ H^+ \Leftrightarrow 4\ Fe(III) + 2\ H_2O\ ,$$

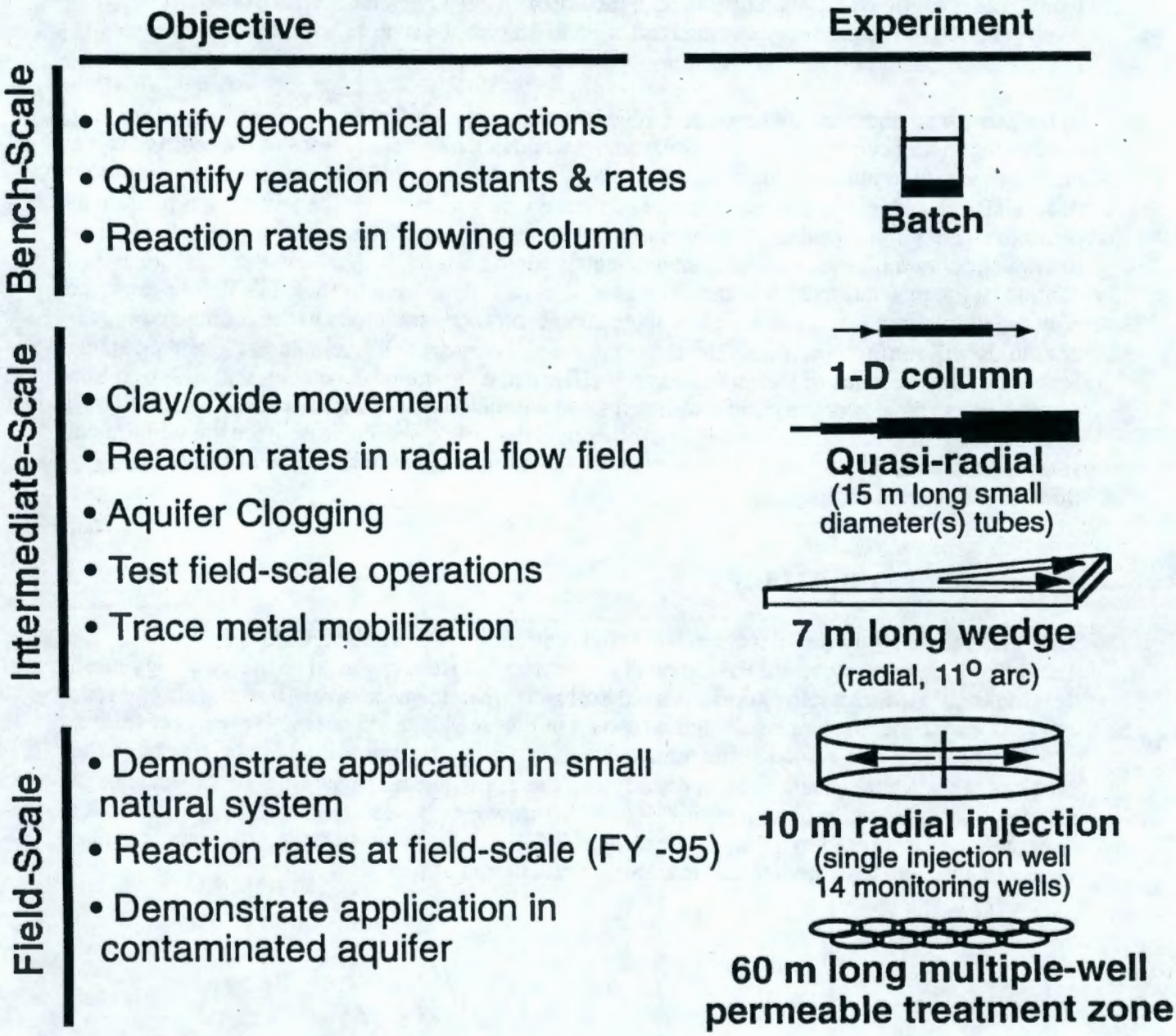
which is very fast. As a result, there will be a deoxygenated plume of groundwater in and downstream of the redox zone. The magnitude of the deoxygenated plume will be diminished from the effects of dispersion and potential mixing of oxygen from the vadose zone. This reoxygenation of the plume is expected to be enhanced near the river as a result of water table fluctuations related to river stage variations.

In the same way that some reduced iron mineral phases are mobilized by reduction reactions (e.g., the iron oxyhydroxides discussed above), other metals in the mineral phases of the sediments may be mobilized by reduction reactions. Additionally, the change in pH and concentration conditions that exist during the injection, residence, and first few pore volumes of the withdrawal phase may result in a change in the adsorption properties of the sediment surfaces, and thus sorbed metals and radionuclides could be released and mobile metals could be sorbed. As the withdrawal stage continues, the injected reagent and buffers as well as any of the mobilized metals will be removed with the withdrawn fluid, and the pH and other concentration conditions in the aquifer sediments and fluids will return to normal. The redox conditions, however, will remain in the altered state because of the presence of the reduced iron [Fe(II)] in the structure of the clay- and silt-sized iron-bearing layer silicates of the aquifer sediments. Any mobilization of metals caused by reactions with the reagent or the altered conditions, other than the redox, should cease once the withdrawal stage is complete (i.e., when 4 to 5 pore volumes of natural groundwater have been flushed through the reacted sediments).

2.2 COMPLETED STUDIES

The ISRM technology was developed by PNNL with funding from the DOE's Office of Technology Development and the Office of Environmental Restoration. The basic strategy used to develop the ISRM technology was a phased approach wherein successively larger scale and more complex experiments were conducted, as shown in Figure 2-1. Each successively larger scale experiment was used to isolate effects related to each scale of experiment and to better design the next larger scale experiment to be undertaken. These experiments ranged from bench-scale batch and column experiments to an intermediate-scale, 7-m wedge (almost field-scale) experiment at Oregon State University to a field experiment at 100-H Area conducted during the summer of 1995. Results of these studies are described in Fruchter et al., 1996.

Figure 2-1. Scale of Experiments Performed in Support of the In Situ Redox Manipulation Experiment Showing the Progression from Bench-Scale Batch Studies Through the 100-H Area Field Experiment. Also shown is the treatability study for the 100-D Area planned for FY 1997.



3.0 PERFORMANCE AND DATA QUALITY OBJECTIVES

The treatability test will provide the necessary data from which to evaluate the viability of the ISRM treatment technology.

3.1 TEST PERFORMANCE OBJECTIVES

Several data quality objective (DQO) workshops were held with the decision makers [DOE, Richland Operations Office (RL), Washington State Department of Ecology (Ecology), and EPA], and the following specific objectives for the treatability test were formulated.

•**Chromate concentration reduction.** The test should demonstrate a quantifiable reduction in the level of chromate contamination in the aquifer.

•**Cost comparisons.** Data need to be gathered to develop a cost model that can be used to compare the ISRM technology against conventional alternatives such as pump and treat. Cost comparisons should be performed on a unit cost basis (i.e., cost per unit mass of chromate reduction). Cost data need to be gathered to determine the economies of scale-up. It was considered that determination of the removal efficiency in percent may be necessary for comparability to other projects. This would be a relative performance standard, rather than a regulatory standard. Costs and efficiency will have to be compared with those of the 100-HR-3 pump-and-treat system. Cost data should be estimated on a total life-cycle cost basis and will include such factors as construction costs, well installation and abandonment costs, sampling and analysis costs, operational and maintenance costs, and costs for re-injection for maintaining the reductive capacity of the treatment zone.

•**Mass reduction.** The test should be conducted on such a scale that a significant reduction in the mass of chromate in the aquifer can be achieved.

•**Implementability information.** The test should be conducted so that the technical feasibility of forming a treatment zone on a large scale can be assessed.

•**Determination of long-term effectiveness**. The test needs to gather data concerning the long-term viability of the technology. The stability of the treatment will be a major measure of success. There would be a determination of whether periodic treatments (i.e., re-injection of reducing agent) were needed. Monitoring intervals for this determination need to be established. Degradation curves, derived from monitoring of water and from soil cores, would provide input data. Bench-scale experiments with sediment collected from the treatment zone will be used to predict long-term performance.

•**Minimizing waste.** The test should be conducted to minimize waste. The treatment zone should be constructed such that it can be part of the large-scale treatment zone if the test proves successful.

•**Evaluation of long- and short-term time factors.** The test should provide information on both the immediate effectiveness of the treatment and the long-term longevity of the treatment. Data for both long term and short term potential side effects of the ISRM technology should also be

gathered and assessed. The side effects include downgradient dissolved oxygen concentrations, aquifer plugging, residual reagents and reaction products, and trace metal mobilization.

•**Community acceptance.** The test should provide enough data so that if the test proves that the technology is both technically and economically feasible, the technology can be presented to the community as an alternative to the conventional treatment methods in the proposed plan.

3.2 DATA QUALITY OBJECTIVES

This section summarizes the decisions that will be made in implementing the ISRM treatability test. Table 3-1 is a "roadmap" of how the treatment barrier will be designed and how its performance will be evaluated. The letter in the fourth column is keyed to Table 3-2. Table A-3 in the Sampling and Analysis Plan (Appendix A) is a set of data sheets that are keyed to these letters. Table A-3 indicates the parameters of interest that will be measured, the analytical method used, and the detection limits. The frequency of measurements is discussed in Section A2.3 of Appendix A.

The detailed design of the ISRM treatability test will be based on data gathered during the pre-design characterization phase of the test. A total of four wells will be drilled during this activity. These wells will be used to gather data regarding the extent of Cr (VI) contamination and to collect data (hydrologic and physical properties of the sediments) to be used for the detailed design of the barrier. Chapter 5.0 describes the drilling strategy and outlines in more detail how the barrier will be designed.

3.3 ANALYSIS REQUIREMENTS AND COMPARISON LEVELS

3.3.1 Statistical Evaluation of Groundwater Data

Statistical methods published by EPA for evaluation groundwater data are designed to (1) compare groundwater data from upgradient and downgradient wells for the purpose of detecting contamination from a waste management unit or (2) compare downgradient wells with a regulatory standard (e.g., maximum contaminant level).

Neither of these methods can be directly employed at the ISRM test site, because it is anticipated that the downgradient concentrations will be profoundly lower than those in the upgradient wells. For this reason, statistics designed to detect small differences in concentrations between wells have little application in this study. If the differences are not large, statistical tests may be needed to compare up- and downgradient compositions, and the tests of type 1 mentioned above are designed to do this. These take the form of the Student's t-test and analysis of variance (ANOVA) tests and are discussed in *Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities* (EPA 1989). Alternatives to these tests are several nonparametric hypothesis tests that compare two or more data sets. These tests include the Wilcoxon Rank Sum, Kruskal-Wallis (for comparison of more than two data sets), and Quantile tests.

3.3.2 Comparison Levels

The Columbia River is the point of compliance for evaluating any effects from the treatment. A chromate concentration of 11 ppb is the target goal in the river. To account for dilution within the aquifer between the monitoring location on-shore and the aquatic receptor exposure point of

concern within the river substrate, a dilution factor of 1:1 is assumed so that 22 ppb would be the goal at the compliance point within the aquifer (reference: Record of Decision for the USDOE Hanford 100-HR-3 and 100-KR-4 Operable Units Interim Remedial Actions). Measurements for chromate, sulfate, and dissolved oxygen between the treatment zone and the river will be major inputs for evaluating the success of the project.

Table 3-1. In Situ Redox Manipulation Key Decisions				
Primary Objective	Decision	Detailed Subobjectives	Activity (See Table 3-2)	Data Analysis Method
Design Barrier	Barrier location	Locate in area of high Cr^{6+} concentration (1,000 ppb)	A	Plot Cr^{6+} concentration on area map
		Locate perpendicular to hydraulic gradient	A	Plot gradient on area map
		Locate in accessible area	Visual & GPR	Plot features on area map
	Dimensions of barrier	Determine radial extent of injection influence	A and B	Reactive Transport injection/withdrawal model
Evaluate Barrier Performance	Laboratory performance	Determine reductive capacity of sediment	J	Measure ability of sediments to reduce Cr^{6+} and Dissolved Oxygen
		Determine reductive efficiency of field method	J	Compare Fe reduction achieved in field with reduction achieved under more favorable laboratory conditions
	Field performance	Spacial distribution of reactive capacity in sediments	J	Spacial plot of microscale laboratory results and lithology. Integrate into an average performance
		Reduction of Cr^{6+}	G and H	Comparison of pre-/post-emplacement and upgradient/downgradient of Cr^{6+}
	Long-term effectiveness[a]	Dissolved O_2 and Cr^{6+} concentration changes	H	Comparison of pre-/post-emplacement and upgradient/downgradient of dissolved O_2 and Cr^{6+} over time
	Side Effects	Aquifer Plugging	G and I	Natural Gradient Tracer Test and Comparison of results of hydrologic tests from before and after emplacement
		Dowgradient Dissolved O_2 impact	G and H	Comparison of pre-/post-emplacement and upgradient/downgradient concentrations
		Trace metals, Residual reagents, Decomposition products, pH	G and H	Comparison of pre-/post-emplacement and upgradient/downgradient concentrations
Economic Feasibility	Economic Evaluation	Design/installation costs	Installation Tracking	Optimize design based on observation of test emplacement and reactive transport modeling
Operation /maintenance costs	Determined from long-term performance	Estimate long-term needs for re-injection of reagent, monitoring	Project Cost Tracking	Budget, schedule, and actual costs will be tracked using Microsoft Project
Cost comparison	Develop cost model for ISRM	Life-cycle cost comparison of ISRM versus pump and treat	Life Cycle Cost Determination	Compare ISRM life cycle costs for comparison with pump and treat systems at the Hanford Site.

[a]Long-term effectiveness will also be assessed by comparing groundwater concentrations of Cr^{6+} and dissolved O_2 up and downgradient from the barrier, reductive capacity of the sediments, and groundwater velocity.

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Table 3-2. In Situ Redox Manipulation Data-Gathering Activities.

Key (See Table 3-1)	Activity	Main Purpose	Data Provided
A	Pre-Design Characterization Wells (4)	Locate barrier, Sediment and chromate characterization of site	Plan view contour maps of chromate and hydraulic head. Aquifer bottom, sediment analysis (porosity, grain size distribution, bulk density), accessible ferric iron and reaction rates, variability in lithology, contaminants of concern (e.g. nitrate)
B	Initial Hydraulic Test	Determine hydraulic properties of aquifer for design analysis	Hydraulic conductivity, specific storage, specific yield, well production rates
C	Injection/Withdrawal and Monitoring Well Installation	Drill wells for barrier emplacement and monitoring (2 Stages of drilling)	Aquifer bottom, variability in lithology (may also need to collect sediment samples to verify parameters collected during Activity A)
D	Background	Determine geochemical conditions at site (pre-emplacement)	Chromate, dissolved oxygen, trace metals, other contaminants of concern
E	Tracer Injection/Withdrawal Test	Determine injection and withdrawal volumes. Pre-emplacement hydraulic properties	Field-scale porosity, injection and pumping volumes and rates. Hydraulic properties
F	Emplacement	Reduce ferric iron in sediment	Dithionite, conductivity, pH, dissolved oxygen in wells. Trace metals and sulfur species in withdrawal water. Criteria analysis for disposal.
G	Post-Emplacement Characterization	Determine hydraulic and geochemical conditions at site (post-emplacement)	Comparison to data from background characterization (Activity E). Chromate, trace metals, residuals (sulfate, sulfite, thiosulfate, carbonate, K, Na), other contaminants of concern, hydraulic properties.
H	Up/Downgradient Chromate Monitoring (ongoing)	Monitor chromate concentrations across barrier	Chromate, dissolved oxygen, pH, conductivity in monitoring wells. Plots of chromate concentrations with time for each well. Upgradient vs. downgradient chromate concentration.
I	Performance Assessment Tracer Experiment	Effectiveness of chromate reduction	Demonstrate travel path through barrier, measure effectiveness of chromate (up vs. downgradient wells), travel time across barrier.
J	Coreholes (4)	Determine effectiveness of reduction - estimate lifetime	Reduction (treatment) capacity of sediment from wells at different locations. Distribution of treatment capacity (pore volumes).

Note: All wells at ISRM site will be measured for hydraulic head, chromate, dissolved oxygen, pH, and conductivity on a Monthly/Quarterly basis after installation to establish baseline data.

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4.0 COMPLIANCE WITH APPLICABLE OR RELEVANT AND APPROPRIATE REQUIREMENTS

In accordance with the EPA's *Guide to Conducting Treatability Studies Under CERCLA* (EPA 1992), onsite treatability tests may be conducted without any federal, state, or local permits (40 CFR 300.400[e][1]); however, such studies must meet applicable or relevant and appropriate requirements (ARARs) under federal or state environmental laws or be exempted by a waiver under CERCLA Section 121(d)(4).

The ISRM treatability test will occur in proximity to the Columbia River [approximately 0.15 km (500 ft)] in an area that is not expected to be culturally and ecologically sensitive. The test requires the construction of groundwater wells. The test also has the potential to generate wastes and wastewater. The major ARARs pertinent to this treatability test are groundwater standards, Columbia River Protection standards, cultural and ecological resource protection requirements, and waste and wastewater management standards.

4.1 GROUNDWATER STANDARDS

The ISRM test will inject and withdraw sodium dithionite into the groundwater to reduce ferric iron in the sediments. Contaminated groundwater currently discharges to the Columbia River. Water quality standards for groundwater (WAC 173-200) and freshwater Ambient Water Quality Criteria (40CFR131.36) will be used to evaluate the performance of the test.

This treatability test will inject a buffered (pH 10.5) sodium dithionite solution into the aquifer. The pH of the aquifer will be temporarily affected (increased to 10.5 for ~24 hr) during the injection and residence stages of the test. The pH will return to normal levels as the majority of the dithionite solution is withdrawn and any residual dithionite is mixed with and diluted by other water in the aquifer. Once the sodium dithionite is withdrawn from the aquifer, the quality of the aquifer will be improved because of the reduction of the chromate and return to normal pH and, therefore, will meet the substantive requirements of WAC 173-218.

4.2 COLUMBIA RIVER PROTECTION STANDARDS

Technology-based limitations and standards, control of toxic pollutants, and monitoring for discharges to waters of the United States, including stormwater, are addressed in 40 CFR 122. Public Law 100-605, *To Authorize a Study of the Hanford Reach of the Columbia River and for Other Purposes*, is applicable to planning, designing, and locating activities in a manner that minimizes direct and adverse effects on the values for which the river is under study.

The treatability test will be conducted within the 1/4 mile limit of the Columbia River. Notification and a request for review and concurrence was sent to the National Park Service by DOE on March 17, 1997. No drilling or other major field activities will be conducted at the site until approval is obtained by the National Park Service. No wastewater discharges to the Columbia River are planned as part of this test. Erosion controls will be used during site preparation and installation of injection/withdrawal wells. The potential for stormwater runoff from the test area is unlikely.

4.3 CULTURAL AND ECOLOGICAL RESOURCE PROTECTION STANDARDS

Cultural resource protection requirements apply because of the potential presence of significant archeological sites or artifacts in the 100-D Area. An initial cultural resource survey has been performed (Appendix B). The *National Historic Preservation Act of 1966* (16 USC 470) is applicable and requires federal agencies to take into account the effect of an activity on any significant cultural resource. The *National Archeological and Historical Preservation Act of 1974* (16 USC 461) is applicable and requires action to recover and preserve artifacts in areas where activity may cause irreparable harm, loss, or destruction of significant artifacts.

The *Endangered Species Act of 1973* (7 USC 136) prohibits activities that threaten the continued existence of listed species or destroy critical habitat. *The Migratory Bird Treaty Act* (16 USC 701-718h) is applicable to protection of migratory birds in the areas. The State of Washington implements the *Bald Eagle Protection Act* (16 USC 668) under the *Bald Eagle Protection Rules* (WAC 232-12-292). These rules are applicable due to the known roosting of bald eagles along the Columbia River. Although threatened and endangered species are known to be present in the 100 Areas, a biological survey has been conducted (Appendix B) and has identified no potential impacts on protected species or critical habitat.

4.4 WASTE AND WASTEWATER MANAGEMENT STANDARDS

The Waste Management Plan for drilling is included in Appendix E of this Treatability Test Plan. Prior to the test, groundwater wells will be installed. Purgewater generated during the development and aquifer testing of these wells that exceed maximum contaminant levels will be contained, transported, treated, and disposed of using the Purgewater Modutanks. Another potential alternative for treatment and disposal of groundwater from aquifer testing during well installations that exceed maximum containment levels would be to use the 100-HR-3 or 100-KR-4 pump-and-treat system as specified in the 100-HR-3 and 100-KR-4 Operable Unit Record of Decision.

During the test, a reagent (sodium dithionite) and pH Buffers (potassium carbonate and potassium bicarbonate) will be injected into the aquifer and allowed to react. Upon completion of the test, approximately five times the injection volume of water will be withdrawn. The withdrawn waters will retrieve all but residual quantities of the unreacted sodium dithionite, its reaction products (sulfate, thiosulfate, sulfite) and pH buffers. Specific injection and withdrawal volumes will be determined following the site characterization and design analysis tasks. The withdrawal water will be placed in Frac Tanks or Modutanks (meeting the substantive requirements of WAC 173-303-630) located near the ISRM project wells. The container contents will be tested to characterize the water for disposal. Trivalent chromium is expected to be the only species of chromium present in the withdrawn water (having been reduced by the injected dithionite). Based upon pre-determined limits defined by the regulatory agencies (Ecology, EPA, and DOE), withdrawal water exceeding a pre-determined limit for sulfate or other constituents will be transported, treated, and disposed at the ETF in the 200-Area. Discharge water below these pre-determined limits, which will be below Hanford Purgewater Criteria at a minimum (WHC, 1990), will be discharged to the ground at a location approved by the regulatory agencies.

All treatability test residuals will be evaluated and managed in compliance with appropriate waste regulations. WAC 173-303 requires the identification and appropriate management of dangerous wastes. WAC 173-304 requires the identification and appropriate management of solid wastes that

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are not dangerous wastes. Wastes generated during the test will be disposed of at the Environmental Restoration Disposal Facility (ERDF), which is designed to meet the substantive standards for disposal of solid and dangerous wastes. Decontamination of equipment will be performed to meet WAC 173-160-530.

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5.0 CONCEPTUAL DESIGN

5.1 PILOT-SCALE BARRIER DESCRIPTION

The pilot-scale permeable treatment barrier in the conceptual design, as shown in Figures 5-1 and 5-2, is 46 m (150 ft) long, 15 m (50 ft) wide, and extends the thickness of the upper unconfined aquifer (~ 5 m or 16 ft). The width and reduction capacity of the barrier controls the volume of upgradient groundwater that will be treated. The length of the barrier is important in this treatability study because it provides some assurance that groundwater monitored downgradient from the barrier has moved through the barrier and has not been bypassed (due to the difficulty in measuring groundwater flow directions at a small scale). The barrier must also be sufficiently large to determine constructability and performance over a large area.

As shown in the initial barrier design in Figure 5-2, the barrier will be created by overlapping five injection/withdrawal operations. Each injection/withdrawal operation will consist of an injection stage, a residence stage to provide time for the reagent to react with the aquifer sediments, and a withdrawal stage to remove any unreacted reagents and degradation products. Groundwater samples will be collected and analyzed during these stages. Each operation will create an effective treatment radius of about 8 m (25 ft) from the injection wells as shown in Figure 5-2. This simple method for barrier emplacement was selected for the following reasons: (1) it provides good recovery of injected reagent and minimizes the volume of wastewater generated; (2) the changing gradients during the injection, residence, and withdrawal stages will enhance the ability of the reagent to invade low-permeability zones within the aquifer; and (3) this method is similar to the field experiment that was conducted at the end of FY 1995 at the 100-H Area. The groundwater flow and reactive transport chemistry of the injection, residence, and withdrawal stages of the barrier emplacement strategy will be modeled prior to emplacement in order to identify important characterization parameters, to refine the emplacement design, and to determine monitoring requirements. This design approach was used in the 100-H Area ISRM field experiment (see Section 9.5).

Additional emplacement approaches will also be investigated to identify/develop a more efficient emplacement design as part of this treatability study. Potential emplacement method alternatives involve the use of more than one well for injection/withdrawal (e.g., Dipole Method). These methods may provide for greater spacing between injection/withdrawal wells than shown in Figure 5-2 and provide for more uniform emplacement of reductive capacity. Issues to be investigated in these alternatives involve limitations of injection extent due to the dithionite reaction rates, volume and composition of reagent, volume and composition of withdrawal water, and requirements for on-site water storage. Because the dithionite/Fe(III) reaction can limit the distance that dithionite can be injected, the amount of Fe(III) in the sediments at the site needs to be adequately characterized across the site in order to pursue various emplacement alternatives. Starting the barrier emplacement for this treatability study with a single well injection/withdrawal ("push-pull") approach will provide more definitive data on the available Fe(III) and reaction rates at the site than can be obtained from laboratory studies of cores. This information is needed for the selection and design of the subsequent phases of injections at the site. The staged schedule for drilling will also allow modifications in well locations to accommodate refinements and modifications from these ongoing characterization and design analysis activities. Interested parties (i.e., Key Decision Makers) will be consulted prior to implementing any proposed changes in the barrier emplacement method.

The wells needed for this treatability study are shown in Figure 5-2. Two types of completed wells are required: 6-in. injection/withdrawal wells and 4-in. monitoring wells. After emplacement is complete, 4-in. coreholes will be drilled to collect sediment samples. The size of the wells indicates the completed well screen size. The total depth of each of these wells and coreholes is approximately 30 m (100 ft). The injection/withdrawal wells are used for the reagent injection and removal. The monitoring wells within the barrier are used to monitor the reagent during the injection/residence/withdrawal stages to determine the extent of the reagent plume created. The coreholes are used to extract sediment samples to determine the reductive capacity of the barrier after emplacement.

In addition to the monitoring wells within the barrier, upgradient and downgradient monitoring wells are required to assess the performance of chromium treatment by the permeable treatment barrier. Chromium concentrations measured in the upgradient monitoring well will be compared to chromium concentrations measured in the downgradient wells. Conservative nonreactive tracers will be added to the upgradient well to verify the travel path through the barrier and determine the arrival time of the water at the downgradient wells. Because of the potential slow groundwater flow velocity at the proposed site, the hydraulic gradients may need to be increased by selective pumping or injection in order to evaluate the effectiveness within a reasonable period of time (i.e., within a year after the barrier is installed).

5.2 WELL INSTALLATION AND EMPLACEMENT STRATEGY

Figure 5-2 shows the initial design and layout for the wells at the 100-D Area site. Drilling will be conducted in four stages as indicated on the diagram. This staged approach to drilling permits the design/well locations in later stages of drilling to be adjusted based on data collected and the characterization and analysis activities conducted in the earlier stages. The flexibility of this approach is particularly important due to the lack of characterization data available in the area around the 199-D4-1 well.

In the first stage of drilling, four pre-design characterization wells will be installed at the site. These wells will be used for physical and chemical characterization of the sediment at the site, determination of hydraulic gradient and hydraulic properties, continuity of the confining layer, determination of concentrations of chromate at the site, and to adjust the final location and orientation of the barrier. In addition to pre-design characterization, these wells will be used during and after emplacement to monitor the performance of the barrier.

The second stage of drilling (see the second group of wells on Figure 5-2) will begin once the pre-design characterization and design analysis is completed. The injection/withdrawal and monitoring wells installed will be used for additional characterization (e.g., tracer test) and the first emplacement at the site to be conducted in FY-97. The first emplacement will be a "push-pull" type, similar to the method used in the 100-H Area ISRM experiment, as discussed in Sections 5.1 and 5.5.3.

Three multi-level piezometers (two depths each) will be installed into the river substrate for additional downgradient monitoring of the ISRM due to the proximity of the proposed ISRM Test site to the Columbia River (~0.15 km [500 ft]). They will be placed along a 150 ft length of the river corresponding to the length of the ISRM barrier. Site characterization data will be analyzed to determine the specific downgradient locations for these piezometers. The piezometers would be installed to collect water samples for measuring the downgradient water quality (e.g., chromate,

dissolved oxygen, sulfate, and trace metals). The piezometers for the river substrate pore water monitoring will need to be installed at a fixed locations for a long-duration (> 3 years) for the purpose of continued monitoring of this treatability study.

The third stage of drilling will be conducted in FY-98 and will finish the installation of the injection/withdrawal and monitoring wells for the pilot-scale barrier. The design and layout for these wells that will complete the emplacement of the treatability test zone may be adjusted based on refinements to the design determined from an analysis of the results from the first emplacement.

The purpose of the fourth stage of drilling is to collect sediment samples from the reduced zone to measure the reductive capacity that was achieved by the treatability study. The analysis of these samples in laboratory column studies will be the basis of the estimate for barrier longevity.

5.3 CHEMICAL REQUIREMENTS

The 100-H Area ISRM proof-of-principle study used an the average concentration of the sodium dithionite in the injection solution of 0.065 molar. The injection solution also contained a pH buffer consisting of 0.26 molar potassium carbonate and 0.026 molar potassium bicarbonate. A conservative tracer (e.g., 100 ppm potassium bromide) was also added to the injection solution. The specific concentrations used in the 100-D Area Treatability Test could vary from that used in the 100-H Area based on the site characterization and design analysis tasks (see Section 9.5). Dithionite and buffer concentrations may also decrease with time during the injection in order to refine the emplacement process. The optimal design would provide for the most efficient use of sodium dithionite by continuously *decreasing* the injection solution concentration as the injection proceeds. Otherwise, if a *constant* concentration is continuously injected, sodium dithionite will eventually be wasted as it is unused by the already-reduced ferrous iron near the well. Refinement of the emplacement process to use lower concentrations of sodium dithionite and potassium carbonate/bicarbonate buffers will help to reduce costs, minimize residual chemicals left in the aquifer, and minimize wastes. Information gathered from the first emplacement process will also be used to refine the later emplacements.

To estimate the volume of sodium dithionite and buffer solution required to create the barrier, the following assumptions/parameters are used:

- 9-m (30-ft) radius of plume to create an 8-m (25-ft) radius reduced zone
- Five overlapping dithionite plumes [at 9-m (30-ft) radius] for a 15-m by 46-m (50-ft by 150-ft) barrier
- Porosity
- Thickness of aquifer
- Sodium dithionite and buffer solution volume for each plume:
  $= \text{porosity} \times \text{thickness} \times \pi \times (\text{radius})^2$.

The porosity and barrier thickness will be determined from the pre-design characterization data and analysis of the tracer test data. Volumes and concentrations of sodium dithionite and buffer solution required will then be estimated from this pre-design characterization data and tracer test analysis.

Experience from the 100-H Area ISRM experiment indicated that about four to five times the injection volume is needed to recover 87 to 90 percent of the unreacted reagent and reaction

products during the withdrawal phase. Better estimates of the required recovery volume will be estimated from the results of the field-scale bromide tracer test at the 100-D Area site. The major ions from the sodium dithionite degradation and reaction products in this withdrawal water include dithionite, sulfite, sulfate, thiosulfate, sodium, potassium, carbonate, and bicarbonate. Dithionite in the withdrawal water will be oxidized quickly after it has been in contact with any sediments containing accessible ferric iron. Under these conditions, dithionite has a first-order decay half-life of up to 10 hr with degradation products of sulfite, thiosulfate, and sulfate. This withdrawal water may also include trace metals mobilized by dithionite from the aquifer sediment (iron, lead, and arsenic) in addition to any local contamination in the 100-D Area groundwater (e.g. tritium, nitrate/nitrite).

5.4 TREATMENT CAPACITY OF BARRIER

The maximum treatment capacity of the barrier will be estimated using analytical data from sediment samples collected at the site during the pre-design characterization stage. The actual treatment capacity will be determined from bench-scale batch or column experiments by circulating oxygen-saturated groundwater with 1,000 ppb chromate through sediment samples from the barrier following emplacement.

Dissolved oxygen, the targeted contaminant (i.e., chromate), and any other consumers of the structural Fe(II) in the reduced zone must be considered when estimating barrier longevity. It should also be noted that for many situations the levels the consumption of structural Fe(II) by the targeted contaminant(s) is small compared to the consumption by the oxygen in natural groundwater. For example in treating a 1-ppm chromium plume, nearly all of the treatment capacity (i.e., the structural Fe(II)) is consumed by the 8 ppm of oxygen typically found in groundwater.

While there are different ways to quantify treatment capacity, a convenient method is to express treatment capacity in terms of the number of pore volumes of oxygenated/contaminated groundwater that must pass through a unit volume of treated aquifer sediments before contaminant breakthrough at levels above those of regulatory concern occurs. Of course, the path through the treated aquifer sediments must be sufficiently long relative to the ambient flow rates and sediment/contaminant reaction rates. Treatment capacity quantified in this manner can be measured by studies on cores of treated sediments using natural oxygenated/contaminated groundwaters. Quantification in this manner also allows the lifetime of the redox barrier to be estimated directly from measure of the ambient groundwater flow rate at the site where the ISRM treatment zone is to be emplaced. Barrier longevity (B_l) in time units can be estimated from the treatment capacity (T_c) in pore volumes, the barrier width (b_w) in length units, and the expected groundwater velocity (v) at the emplacement location by the following equation.

$$B_l = T_c * b_w / v$$

For example, if an ISRM zone 15 m (50 ft) wide was emplaced with a treatment capacity of 70 pore volumes (based on the results of the 100-H Area ISRM Proof-of-Principle Field Test) in an area where the groundwater flow rate was 15 m (50 ft)/yr then the estimated lifetime of the barrier would be ~70 years.

The thickness of the barrier multiplied by the number of pore volumes of treatment capacity within the barrier yields the upgradient distance from the barrier of groundwater that could be treated as depicted in Figure 5-1 (assuming a uniform aquifer thickness and that the contaminant does not sorb onto the sediment, i.e., that it travels in the groundwater at the same rate as dissolved oxygen). Therefore, a 15-m- (50-ft) wide barrier with a 70 pore volume treatment capacity would be capable of treating groundwater up to 1,050 m (3,500 ft) upgradient from the barrier. Treatment distances greater than the current length of a groundwater plume may be desirable to treat continuous sources feeding the plume at the surface or in the vadose zone.

Most estimates of groundwater velocity around the 100-H Area are in the 0.3-m/day (1-ft/day) range. Using the 0.3-m/day (1-ft/day) value, one pore volume would move through a 15-m- (50-ft) wide barrier every 50 days. Multiplying this time by the treatment capacity of the barrier (using the 70 pore volume estimate of treatment capacity from the 100-H Area test) results in an expected barrier lifetime of about 10 years. Detailed characterization of the iron content, hydraulic properties, and the efficiency of iron reduction by ISRM at the selected 100-D Area site is needed (and planned) to estimate the treatment capacity and expected lifetime of the emplaced permeable treatment barrier. The maximum treatment capacity and barrier lifetime at the 100-D Area is expected to be greater than at the 100-H Area ISRM site because the Ringold Formation sediments (forming the unconfined aquifer at the D-Area) generally have greater contents of available Fe(III) than Hanford Formation sediments (forming the unconfined aquifer at the H-Area) and groundwater flow rates at the 100-D Area (~ 8 to 15 m/yr [25 to 50 ft/yr]) are less than at the 100-H Area (~110 m/yr [365 ft/year]).

5.5 ISRM TREATABILITY TEST ACTIVITIES

This section describes the specific tasks that will be performed to complete the treatability test. The tasks correspond to the those presented with the DQOs in Section 3.0. These activities have been condensed to include design analysis, field characterization, permeable treatment barrier emplacement, and barrier performance assessment and monitoring.

5.5.1 Design Analysis

Data-gathering activities to support design analysis consist of the characterization wells, first and second groups (Activity A), and the initial hydraulic testing (Activity B) (Table 3-2 and Appendix A).

5.5.1.1 Pre-design Characterization Wells. Four wells will be drilled to determine the variations in chromate concentrations, the amount of reducible iron in sediment, aquifer thickness, and direction of hydraulic gradient to establish the location and orientation for emplacement of the barrier. These characterization wells will also be used to monitor emplacement of the barrier. Bench-scale column experiments will be conducted with sediments collected from the aquifer at the site using the target concentration of sodium dithionite and buffer to estimate reaction rates and the available Fe(III) in the sediments.

5.5.1.2 Hydraulic Testing. Hydraulic testing will be performed to determine hydraulic properties of the aquifer. Data obtained from drilling the pre-design characterization wells will be evaluated to determine which well(s) will be tested. Numerical modeling integrating site data and experimental results to test and refine the barrier emplacement design will then be performed.

5.5.2 Field Characterization

The field characterization task involves drilling the injection/withdrawal and monitoring wells (Activity C) as shown in the conceptual design in Figure 5-2, collecting background samples (Activity D), and performing the injection/withdrawal tracer test (Activity E).

5.5.2.1 Injection/Withdrawal and Monitoring Well Installation. The layout of the injection/withdrawal and monitoring wells is shown in Figure 5-2. Exact locations and depths of these wells will be determined once the pre-design characterization wells have been drilled. Additional characterization data will be collected during the drilling of the injection/withdrawal wells. The extent of the characterization will depend on results of the pre-design characterization effort. Other aquifer testing will be conducted as part of the tracer test phase.

5.5.2.2 Background Sampling. Water quality testing will be performed to establish a baseline before barrier emplacement. Details of this testing are presented in the Sampling and Analysis Plan (Appendix A).

5.5.2.3 Injection/Withdrawal Tracer Test. An injection/residence/withdrawal tracer test will be conducted at the site with a nonreactive, conservative tracer (i.e., Bromide) prior to the injection/withdrawal of dithionite. The results of the tracer test will be used to determine the larger scale porosity of the aquifer, the amount of sodium dithionite required for injection, the amount of wastewater generated during the withdrawal, and the rates and durations needed for injection and withdrawal.

The tracer test will be conducted on the center injection/withdrawal well. Additional tracer tests may also be required on other injection/withdrawal wells based on observations of variations in lithology.

Aquifer testing is required to determine injection and withdrawal rates and to identify any large-scale heterogeneous zones within the barrier. These tests include short-duration pumping tests immediately following well completion to determine well performance characteristics (specific capacity) followed by slug interference and/or constant rate discharge tests to determine site-scale hydraulic properties.

The information obtained from the tracer test will be incorporated into a numerical model developed to simulate site-specific transport processes and aid in the evaluation and improvement of the design of the dithionite injection/withdrawal. The tracer experiment will help determine the volume of injection fluid required to create a 9-m (30-ft) radial plume and the withdrawal volume required to recover the injected conservative tracer and thus the injected reagent and reaction products from the barrier. The tracer experiment will also help fine-tune the sampling strategy (starting sampling time, sample volume, and sample frequency required at each location) and trouble-shoot systems (i.e., injection/withdrawal system equipment, sampling pumps, flowthrough cells, bromide probes, mixing tank). A general description of the tracer test is given in the following paragraphs.

For the injection/withdrawal tracer test, a potassium bromide solution (~100 ppm bromide) will be injected into the center injection/withdrawal well. Water for the solution will be pumped from the aquifer prior to the injection. The injection could last up to 24 hrs, depending on the onsite tracer solution storage capacity and the time required for the tracer to reach a 9-m- (30-ft) radius based on

estimates made regarding tracer arrival at the monitoring wells. A set of baseline water samples will also be collected prior to injection.

During the tracer test, several groundwater parameters will be monitored using a flowthrough chamber and selected probes. Parameters to be monitored include pH, temperature, conductivity, dissolved oxygen, and bromide concentration; in addition, samples will be collected for laboratory analysis of bromide concentration.

Sample collection frequency and location will be determined based on final locations of monitoring wells and observations in lithology. Sampling frequency and duration will be dependant on radial distance from the point of injection. The monitoring well(s) nearest the injection well will initially be assigned a sampling interval. This sampling interval will continue until bromide has arrived at the closest monitoring wells, at which time sample collection will be initiated in monitoring wells located further (radially) from the injection/withdrawal well. Periodic sampling will be conducted at all wells to account for unpredicted behavior due to heterogeneities. Samples will be collected from these monitoring wells as required to describe the movement of the tracer front. The sampling interval for each monitoring well will be based on simulated response and adjusted in the field as necessary.

A residence phase of approximately 18 hr will follow the injection to determine the effects of drift at the site. After the residence phase, the bromide will be pumped out at a rate similar to the injection rate until the concentration in the withdrawal water is near background. Simulations show that about four times the injection volume is required for withdrawal, but heterogeneities and sorption of some of the injected reagent during barrier emplacement could increase the withdrawal volume. The tracer study should be able to isolate the withdrawal effects due to heterogeneities.

The withdrawn water containing bromide will be handled in accordance with the purgewater strategy (see Section 11.0). During the withdrawal phase, samples will be collected from monitoring wells and the withdrawal stream as required to describe transport of the injected tracer back to the injection/withdrawal well. The sampling strategy during the withdrawal phase will initially be based on simulated response and adjusted in the field as necessary.

5.5.3 Permeable Treatment Barrier Emplacement

This task consists of emplacing the permeable treatment barrier (Activity F) through five consecutive injection/residence/withdrawal stages in the injection wells shown in Figure 5-2.

5.5.3.1 Emplacement Process. As discussed previously, emplacement using the initial design consists of emplacing the barrier (injection stage), allowing time for the reagent to react with aquifer sediments (residence stage), and removing any unreacted reagent and/or degradation products (withdrawal stage).

Injection - During the injection stage (estimated to take ~24 hr per injection/withdrawal well), the reagent will be injected through each of the injection/withdrawal wells, one at a time, at a rate to be determined by field characterization data. Estimates of the injection volume will be made once the bromide tracer field experiment has been conducted.

Residence - The residence stage provides additional time for the reagent to react with the aquifer sediments. The duration of this stage will be ~18 hr.

Withdrawal - During the withdrawal stage, any unreacted reagent, mobile reaction products (sulfites, thiosulfate, and sulfate), and any mobilized species (e.g., iron and other metals) will be pumped from the aquifer. The 100-H experiment required about five times the injection volume of water to recover about 90% of the reagent, tracer, and buffers. The volume can be influenced by heterogeneities at the site. Better estimates of the required recovery volume (as has been discussed) can be calculated based on the results of the field-scale bromide tracer test once it is completed.

During each stage of the emplacement process, sampling and monitoring will be performed on the solutions collected from the injection wells, the feed tank, the monitoring wells, and the overlapping injection wells. These samples will be analyzed for dithionite concentrations and other parameters as discussed in the Sampling and Analysis Plan (Appendix A).

The emplacement strategy has been developed to minimize the number of monitoring and injection/withdrawal wells (Figure 5-2). This strategy features the following:

- Successive reduction in the number of monitoring wells required for each injection/withdrawal process will help determine minimum number of wells for expandability of barrier
- Injection/withdrawal begins at center working outward on alternating sides for the first three injection/withdrawal processes.
- Central upgradient and downgradient monitoring wells are close to the barrier to provide short travel times for performance monitoring.
- Central upgradient and downgradient monitoring wells are 4-in. diameter to serve a dual purpose of providing for hydraulic testing (on the upgradient side) and gradient control (to increase travel times if needed).
- The injection/withdrawal process will be monitored from adjacent injection/withdrawal wells.

5.5.4 Barrier Performance Assessment and Monitoring

This task involves the evaluation of the permeable treatment barrier in its effectiveness in chromium remediation, impact on the water quality, and long-term capacity. The project stages included are post-emplacement characterization (Activity G), upgradient/downgradient monitoring (ongoing) (Activity H), performance assessment tracer experiment (Activity I), and coreholes (Activity J).

5.5.4.1 Post-Emplacement Characterization. After the barrier is emplaced, hydraulic testing is needed to determine if any detectable changes occurred to the hydraulic properties of the barrier/aquifer. The water quality downgradient from the barrier will also be monitored.

5.5.4.2 Upgradient/Downgradient Monitoring and Performance Assessment Tracer Experiment. As the main measure of the effectiveness of chromium remediation for the permeable treatment barrier, chromium concentrations will be monitored in the upgradient and downgradient monitoring wells. Tracers will be added to the upgradient well to determine the arrival of the upgradient water in the downgradient monitoring wells and to demonstrate the travel path through the barrier. Because of the slow estimated groundwater velocity in the region around the barrier, about 8 to 15 m/yr (25 to 50 ft/yr), some hydraulic control through the use of pumping

or injection may be required to shorten the travel time from the upgradient to downgradient wells. The downgradient wells will be a sufficient distance from the barrier to avoid any influences from the barrier emplacement.

5.5.4.3.3 Coreholes. After the injection/residence/withdrawal operation has been completed at all five injection wells, sediment samples will be collected by coreholes drilled within the barrier as shown in Figure 5-2. This sediment will be analyzed to determine the reductive capacity of the sediments within the barrier. This will be accomplished by batch and column studies of the sediment to determine the overall treatment capacity of the reduced sediment within the barrier.

Additional coreholes should be collected from the fringe and interior of the barrier at least 1 yr after the barrier emplacement in order to measure the loss of treatment capacity through bench-scale experiments. These additional coreholes are not shown in Figure 5-2.

Figure 5-1. Conceptual Plan View of ISRM Treatment.

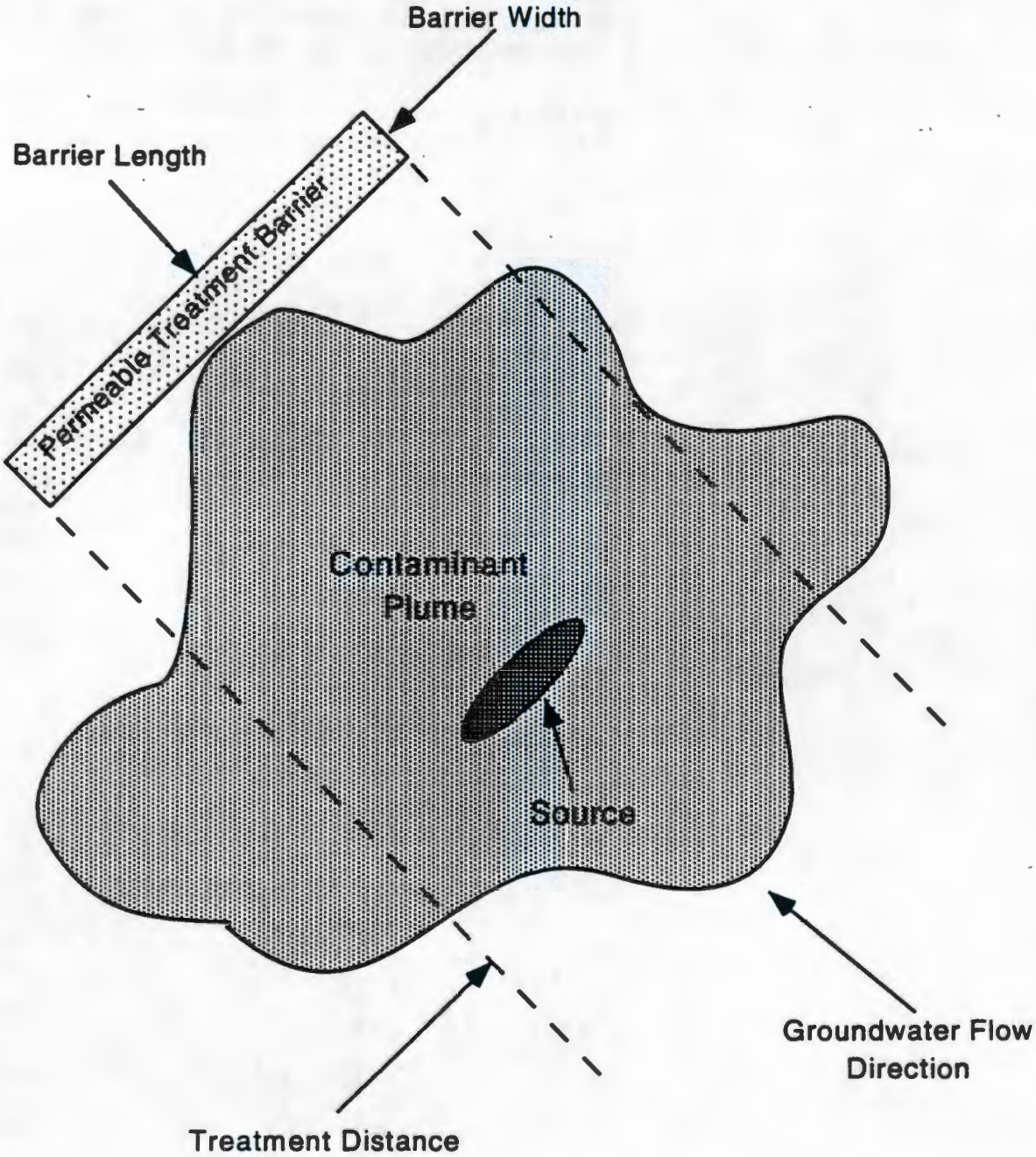

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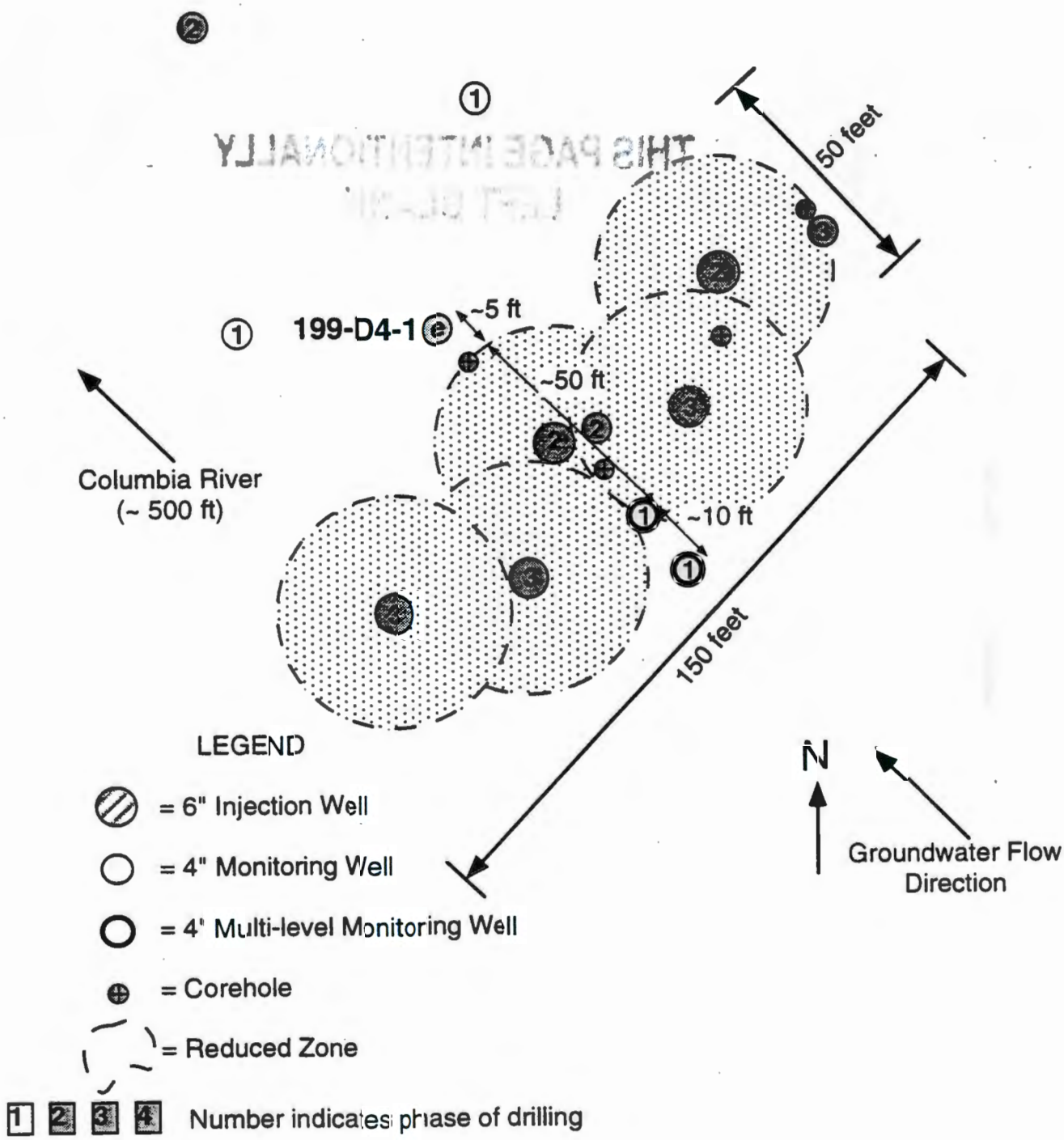
Figure 5-2. Conceptual Design of ISRM Permeable Treatment Barrier.



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6.0 EQUIPMENT AND MATERIALS

This section presents the field equipment and materials needed to emplace the ISRM barrier.

The conceptual layout of the ISRM field site is shown in Figure 6-1. Until the design analysis and field characterization phases of the treatability test are complete, equipment cannot be sized and volumes of material required cannot be determined.

The buffered reagent solution (sodium dithionite plus potassium carbonate and potassium bicarbonate) will be delivered premixed, in a concentrated liquid form. The injection solution will consist of an aqueous buffered reagent solution. The concentration of the injection solution will be determined after the design analysis and field characterization have been performed.

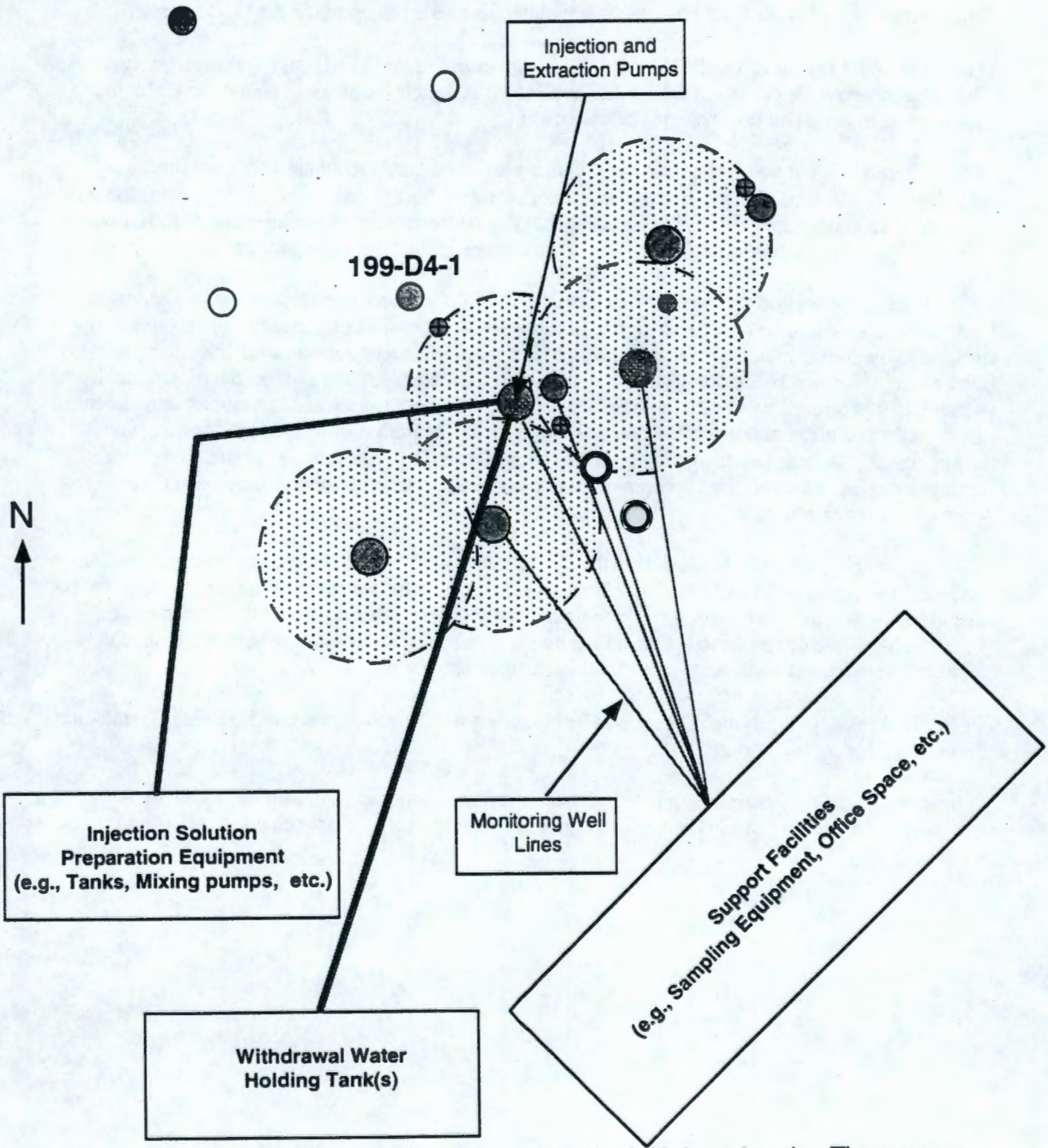
One of the objectives of the barrier emplacement design is to minimize the amount of sodium dithionite injected. The optimal design would provide for the most efficient use of sodium dithionite by continuously *decreasing* the injection solution concentration as the injection proceeds. Otherwise, if a *constant* concentration is continuously injected, sodium dithionite will eventually be wasted as it is unused by the already-reduced ferrous iron near the well. Continuous adjustment of the injection solution concentration can be accomplished through a variety of surface equipment arrangements. A detailed design analysis will be performed to determine the optimal equipment arrangement once the required sodium dithionite concentrations and volume have been determined from characterization data.

All water withdrawn from wells during the ISRM test will be held in a temporary storage container (meeting the intent of WAC 173-303-630) for analysis prior to treatment, transport, or disposal (as discussed in Section 4.4). The storage container will be sized after sodium dithionite injection volumes have been determined. Depending on the volume of water to be withdrawn from each injection/withdrawal well, multiple storage containers may be necessary.

Vessels containing dithionite reagent will be blanketed with argon to prevent dithionite degradation before and during injection.

During and following barrier emplacement, all injection/withdrawal and monitoring wells will be equipped with packers or blanketed with argon to keep atmospheric oxygen from diffusing into the wellbore.

Figure 6-1. In Situ Redox Manipulation Field Site Conceptual Layout.



Note: This diagram shows the setup for only one injection/withdrawal cycle. The process will be conducted sequentially on each injection/withdrawal well.

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7.0 SAMPLING AND ANALYSIS

As discussed in Section 5.0, sampling will be performed throughout the various stages of the ISRM treatability test. The Sampling and Analysis Plan (SAP), which includes the Field Sampling Plan (FSP), is presented in Appendix A.

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8.0 DATA MANAGEMENT

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 environmental samples. The data will be stored electronically in Microsoft Excel spreadsheets and paper copies will be maintained in the project files. A project data custodian will be designated to control and maintain the data. The following data will be contained, at a minimum, as part of the database:

- Sample identifier
- Sample location
- Sample medium type
- Sampling date
- Analysis date
- Laboratory name
- Analyte name
- Concentration value
- Measurement unit

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9.0 DATA ANALYSIS AND INTERPRETATION

Detailed discussions of the planned tests and sampling are found in Chapters 3.0 and 7.0. This chapter describes the plan that will be used for the analysis of the performance monitoring data. The planned ISRM performance monitoring and testing program includes:

- Establishing pre-emplacement Cr^{6+}, water quality, and aquifer characteristics at the test site to enable interpretation of ISRM performance
- Pre- and post-construction hydrologic testing at the site to determine the hydrologic properties of the ISRM treatment zone relative to the natural aquifer sediments
- Performing routine performance monitoring of Cr^{6+} and water quality at the test site for evaluation of ISRM performance
- Conducting tracer test to determine the path and travel time through the ISRM treatment zone, as well as to support Cr^{6+} performance evaluation
- Collecting aqueous samples on a periodic basis to assess any impacts on the aquifer or degradation of the ISRM treatment zone
- Collecting sediment from ISRM treatment zone for bench-scale tests to predict treatment capacity.

This chapter describes the analysis of data to interpret the performance of the ISRM treatment zone. The analysis can be viewed in terms of assessing barrier performance in four areas of functionality: (1) laboratory-scale performance (i.e., maximum theoretical performance ignoring effects of heterogeneities in the emplacement, wall effects, short circuiting, channeling); (2) field performance (i.e., performance as emplaced quantifying the effects of heterogeneities in the emplacement, wall effects, short circuiting, channeling); (3) long-term effectiveness of the treatment zone; and (4) side effects (i.e., quantify the effect the treatment zone has on the chemistry of the aquifer). Design of the barrier is the goal of a separate characterization effort and is described in Section 9.5.

A combination of hydrogeologic and chemical analyses will be performed to make these assessments. The hydrologic analyses will identify how groundwater is affected by the treatment zone, and the chemical analyses will identify how efficiently the treatment zone reduces the chromate. The overall performance of the technology will be judged by the combined effectiveness of these mechanisms.

9.1 BENCH-SCALE PERFORMANCE

The assessment of bench-scale performance will be based primarily on determining the ability of the reduced sediments to reduce chromate and the reductive capacity of the sediments after treatment as compared to the reductive capacity achieved under more favorable laboratory conditions. Bench-scale capacity to reduce chromate will be assessed by using core samples taken from within the treatment zone to reduce chromate in the laboratory.

Maximum reductive capacity of the sediments will be assessed by subjecting core samples to dithionite treatment and comparing the chromate treatment capacities of the sediments before and after laboratory dithionite treatment. This will allow for an assessment of the efficiency of the reduction by the field method.

9.2 FIELD PERFORMANCE

The assessment of field performance will be based on determining the spacial distribution of the reactive capacity of the sediments and by comparing the upgradient and downgradient chromate concentrations. A spacial plot of the reductive capacity will be prepared and used to define an average performance of the treatment zone. Where possible, the limited core and soil data (porosity, grain size distribution, and bulk density) will be used with drilling logs to characterize large-scale stratigraphic features at the site. This information may be used to identify features that could impact the performance and monitoring of the ISRM.

9.3 LONG-TERM PERFORMANCE

Long-term performance will be assessed by comparing the upgradient and downgradient concentrations of chromate and dissolved oxygen. Periodic groundwater samples will be collected over the course of a few years to possibly determine a trend in these concentrations and to predict the long-term viability of the treatment zone. Because of the estimated lifetime of the barrier (~10's years), the lifetime of the barrier cannot be determined by field observations over a much shorter duration. Therefore, the barrier lifetime will be estimated from treatment capacity measured in the laboratory from sediment samples collected from the reduced zone.

9.4 SIDE EFFECTS

Side effects include potential plugging of the aquifer, changes in aquifer chemistry (such as dissolved oxygen and pH), mobilization of trace metals, and residual reagents and decomposition products. These issues were also addressed in the 100-H ISRM field experiment (see Fruchter et al., 1996).

Aquifer plugging will be assessed by comparing the results of aquifer hydraulic characteristic tests before and after emplacement of the treatment zone. Hydraulic head, hydraulic conductivity, and storativity estimates will be compared to quantify any changes in hydraulic properties caused by barrier emplacement.

Concentrations of key parameters will be measured in the aquifer to assess the effect of the treatment zone on the aquifer chemistry. Chromate, pH, dissolved oxygen, conductivity, sulfate/sulfite, inductively coupled plasma (ICP) metals, and concentrations of specific anions will be measured (see Table A-3 in Appendix A for a complete list of analytes).

Due to the proximity of the test site location to the Columbia River, a contingency has been developed in the event that the dissolved oxygen concentrations are severely reduced in the groundwater entering the river. This will be determined by the concentrations observed in the farthest downgradient monitoring wells from the ISRM zone. The contingency involves the

initiation of pumping of groundwater from the injection/withdrawal wells and downgradient monitoring wells at the site (e.g., well 199-D4-1) in order to rapidly re-oxygenate the reduced zone to stop any additional groundwater with low dissolved oxygen concentrations from entering the river. The pumping will stop once the dissolved oxygen concentrations at the site are back to pre-emplacement levels.

9.5 DESIGN ANALYSIS

The design analysis will determine the parameters needed for the barrier emplacement (see Figure 9-1). These parameters include injection well spacing, dithionite and buffer concentrations for injection, injection and withdrawal rates, injection and withdrawal volumes, duration of reaction stage, and an estimate of the amount of reduction of ferric iron from the emplacement. The design analysis process integrates the site characterization data using numerical models. The site characterization data will be incorporated into these numerical models to simulate the dithionite injection, reaction, and withdrawal stages of the emplacement.

Two numerical models will be used as part on the design analysis. The first model to be used is a one-dimensional, radial, reactive transport computer code that was developed as part of the ISRM project last year. This code simulates the redox and degradation reactions of the injection of sodium dithionite and pH buffers into the aquifer. The rates of the reactions can be approximated by pseudo-first-order kinetics based on the results of batch and intermediate-scale experiments conducted over the past few years. The testing of the applicability of this code to the 100-H Area field experiment is currently under way. The reaction rates will also be determined for the Ringold sediment at the selected 100-D Area field site. The reaction rate of the reduction of ferric iron by sodium dithionite is short (~5 hr) in relation to the travel time to inject reagent to a target distance of 15 m (25 ft) (~18 hr). Therefore, a large excess of accessible ferric iron can inhibit the ability to reduce sediment at a large distance from the injection well. Using the pre-design characterization data, a number of different combinations of injection rate, injection duration, and injection concentration (varying during the course of the injection) will be investigated using this reactive-transport code. A strategy of multiple injection/withdrawal of reagent at one location may also need to be pursued. These simulations will determine the parameters needed to reduce sediment out to the target radial distance from the injection/withdrawal well. The spacing of injection wells will be based on the radial extent of the reduced zone in the design and will provide for overlap between the reduced zones.

A second numerical model will be used in the design analysis to simulate more complex hydrologic processes. Specifically, this model will be used to simulate the transient transport effects of the mounding of the water table during injection and the pumping cone-of-depression formed during the withdrawal. This model will help predict the amount of reagent that is transported to the injection mound (above the ambient water table) during the injection and the impact on recovery of reagent and reaction products during the withdrawal stage by the slow drainage of reagent trapped in the vadose zone by the injection mound. Although strongly influenced by heterogeneities, the rate and duration of withdrawal will also be estimated from this modeling activity. This model will also help in determining the sampling timing and frequency at the observation wells.

Heterogeneities will be addressed by sensitivity modeling using the ranges in parameters measured from the boreholes at the site (e.g., reactable iron, porosity). The distribution of these parameters will be inferred from the lithologic description matched to the limited number of sediment samples that will be analyzed in the laboratory for physical and chemical properties. The final design will

be based on a reasonable distribution of properties at the field site. The design will be tested at the field site by the tracer test and the emplacement strategy (i.e., additional monitoring wells in the first dithionite injection/withdrawal), as discussed in Section 5.3.3.1.

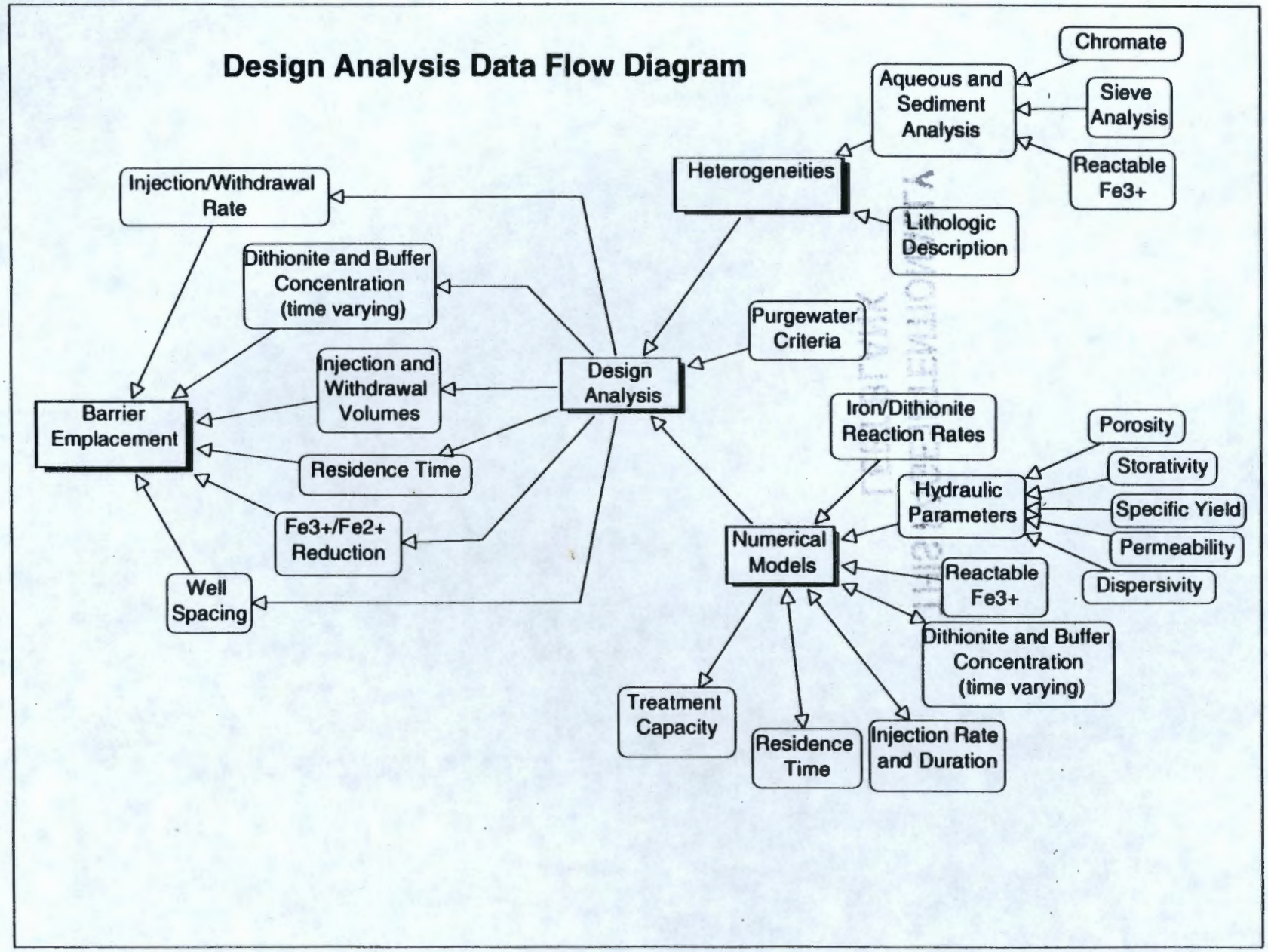

Figure 9-1. ISRM Design Analysis Flow Diagram.

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10.0 HEALTH AND SAFETY

Safety and health issues relating to the treatability test are addressed in site-specific safety documents that identify both radiological and industrial safety and health hazards as well as control measures for those hazards. Safety documents include specific training requirements for all site workers as well as visitors. Job-specific Health and Safety plans have been prepared for the drilling activities. A Health and Safety Plan covering the emplacement procedures was developed for the 100-H Area Experiment and will be modified for applicability to the 100-D Area Treatability Study. This Health and Safety Plan will be included in the appendix of the final version of this test plan.

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11.0 RESIDUALS MANAGEMENT

Management of residuals (soil and water samples and drill cuttings) relating to the well and corehole drilling for this treatability test are addressed in the Waste Management Plan in Appendix E. Management of residuals as part of the emplacement (only water samples will be generated during this process) will be conducted as described in the Waste and Wastewater Management Section above (Section 4.4).

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12.0 QUALITY ASSURANCE

All work conducted by the Pacific Northwest National Laboratory (PNNL) shall be performed according to appropriate standards of quality, reliability, environmental compliance, and safety based on client requirements, cost and program objectives, and potential consequences or malfunction or error. To provide clients with quality products and services, PNNL has established and implemented a formal Quality Assurance (QA) Program. These management controls are documented in the PNNL Standards-Based Management System (SBMS) and the Quality Assurance Manual (PNL-MA-70) and its accompanying standards and procedures. The QA Program is based upon the basic requirements and supplements of ASME NQA-1 (1989), Quality Assurance Program Requirements for Nuclear Facilities, as interpreted for PNNL activities. Additionally, the quality requirements are augmented to include the Total Quality approach defined in the Department of Energy Order 5700.6C/10 CFR 830.120, Quality Assurance. The QA Plan for sampling and analysis is contained in Appendix A.

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13.0 COMMUNITY RELATIONS

The DOE, Ecology, and EPA developed a Community Relations Plan in April 1990 as part of the overall Hanford Site restoration. The Plan was designed to promote public awareness of the investigations and public involvement in the decision-making process. The Plan summarizes known concerns based on community interviews. Since that time several public meetings have been held and numerous fact sheets have been distributed in an effort to keep the public informed about Hanford cleanup issues. The Plan was updated in 1993 to enhance public involvement and is currently undergoing an additional update.

The 100 Area Focused Feasibility Study Document (DOE-RL 1995a) and Proposed Plan for 100-HR-3 (DOE-RL 1995b) were made available to the public in both the Administrative Record and the Information Repositories. These documents underwent a 45-day public comment from September 11, 1995 to October 25, 1995. "Tests to Immobilize Chromium in the Aquifer" were described in general terms in the Proposed Plan for 100-HR-3.

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14.0 NEPA VALUES

In accordance with DOE Order 451.1 and DOE Secretarial NEPA Policy, DOE CERCLA documents are to incorporate *National Environmental Policy Act of 1969* (NEPA) values to the extent practicable. NEPA values, such as analysis of cumulative offsite ecological and socioeconomic impacts, description of the affected environment (including meteorology, hydrology, geology, cultural and ecological resources, and land use), short-term and long-term impacts on human health and the environment, emissions to air and water, and cost, are typically included in CERCLA feasibility study.

Several NEPA values common to all of the 100 Area operable units, including laws and guidelines, are addressed in the *100 Area Feasibility Study Phases 1 and 2* (DOE-RL 1993). NEPA values associated with ISRM treatability test were evaluated in the *100-HR-3 Operable Unit Focused Feasibility Study* (DOE-RL 1995a).

NEPA values specific to the ISRM project are as follows.

- Cultural and ecological resources' reviews were performed in support of the ISRM project (Appendix B). The survey reports indicate that the area where the in situ test is to occur has been previously disturbed. No cultural resources are reported or anticipated with the project area.

- Particulate releases to the atmosphere would be limited to fugitive dust emissions that might occur as a result of the proposed activities (e.g., movement of vehicles and equipment). The Columbia River is located at least 0.15 km (500 ft) from the proposed the ISRM project area; care would be taken to minimize the chance of the river becoming a consequential pathway for particulates.

- Droplet releases might result from the use of uncontaminated water, which would be applied as necessary to mitigate dust during the well installations and construction of the ISRM project.

- Removal, storage, and disposal of waste would be in accordance with applicable federal and state regulations and guidelines and would not impact employees or the environment.

- The proposed activity is 0.15 km (500 ft) from the Columbia River. Public Law 100-605, *Study of the Hanford Reach of the Columbia River,* requires notification of the National Park Service (NPS) of the U.S. Department of the Interior if the project is to be conducted within 1/4 mile of the Columbia River. Since the project is at a location within the 1/4-mile limit, the NPS will be notified of the project so that a review can be completed. Any NEPA mitigation measures identified by NPS will be incorporated into the project plan. Standard construction practices would prevent adverse impact to the 100-yr floodplain or wetlands. Precautions will be taken to ensure that stormwater runoff from the construction area does not enter the river.

- The ISRM project represents a small fraction of the total Hanford budget. Therefore, the project is not expected to impact socioeconomics of the Tri-Cities or other parts of Benton and Franklin Counties.

- The project staff and materials associated with the ISRM project would not significantly impact transportation in the area.

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15.0 REPORTS

A test report summarizing the results of the treatability test will be prepared. The format of the report will be based on the suggested outline for treatability test reports provided in the *Guide for Conducting Treatability Studies Under CERCLA* (EPA 1992). Project briefings will be given at unit manager meetings between DOE and the regulators.

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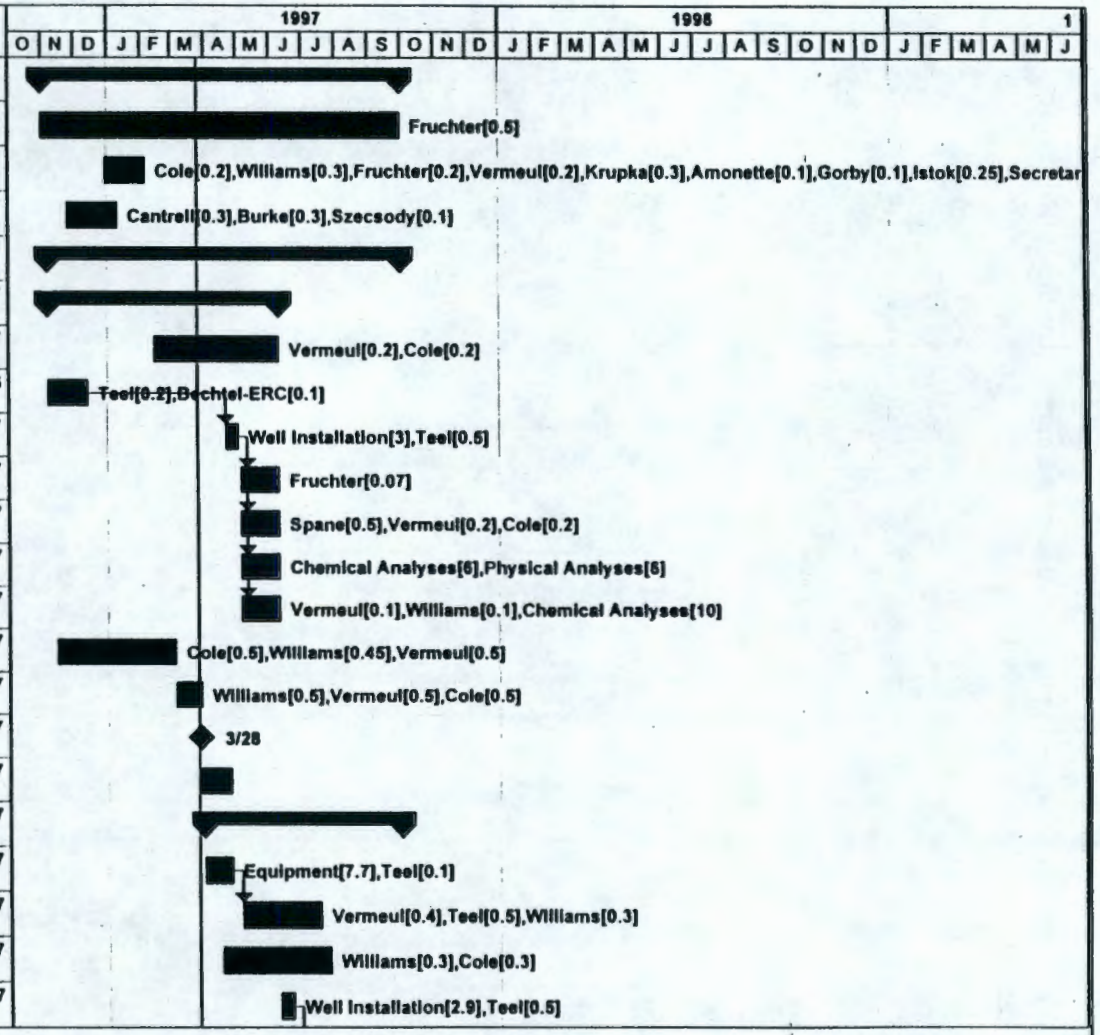
16.0 SCHEDULE

The current project schedule shown in Figure 16-1 lists key activities for the ISRM project. The schedule shows durations of each major activity.

Table 16-1. ISRM Treatability Test Project Schedule.

ID	Task Name	Start	Finish
1	Management	Fri 11/1/96	Tue 9/30/97
2	Task Management	Fri 11/1/96	Tue 9/30/97
3	Peer Review	Mon 12/30/96	Wed 2/5/97
4	Uranium Experimen	Mon 11/25/96	Fri 1/10/97
5	Support 100D Treatabil	Thu 11/7/96	Wed 10/1/97
6	Pre-Injection Char	Thu 11/7/96	Mon 6/9/97
7	Field Support -	Fri 2/14/97	Mon 6/9/97
8	Prepare Drillin	Thu 11/7/96	Fri 12/13/96
9	Drill Wells - Ph	Mon 4/21/97	Fri 5/2/97
10	Chromate Anal	Mon 5/5/97	Mon 6/9/97
11	Hydraulic Test	Mon 5/5/97	Mon 6/9/97
12	Physical An	Mon 5/5/97	Mon 6/9/97
13	Well Monitori	Mon 5/5/97	Mon 6/9/97
14	Design Analysi	Fri 11/15/96	Tue 3/4/97
15	Finalize Test P	Wed 3/5/97	Fri 3/28/97
16	Submit Test Pl	Fri 3/28/97	Fri 3/28/97
17	Test Plan Appr	Fri 3/28/97	Thu 4/24/97
18	Construction and	Mon 3/31/97	Wed 10/1/97
19	Procure Equip	Mon 3/31/97	Fri 4/25/97
20	Set Up Equipm	Mon 5/5/97	Wed 7/16/97
21	Field Support -	Wed 4/16/97	Fri 7/25/97
22	Drill Wells - P	Mon 6/9/97	Fri 6/20/97



Project: Redox97
Date: Tue 3/25/97

Task | Progress | Milestone | Summary | Rolled Up Task | Rolled Up Milestone | Rolled Up Progress

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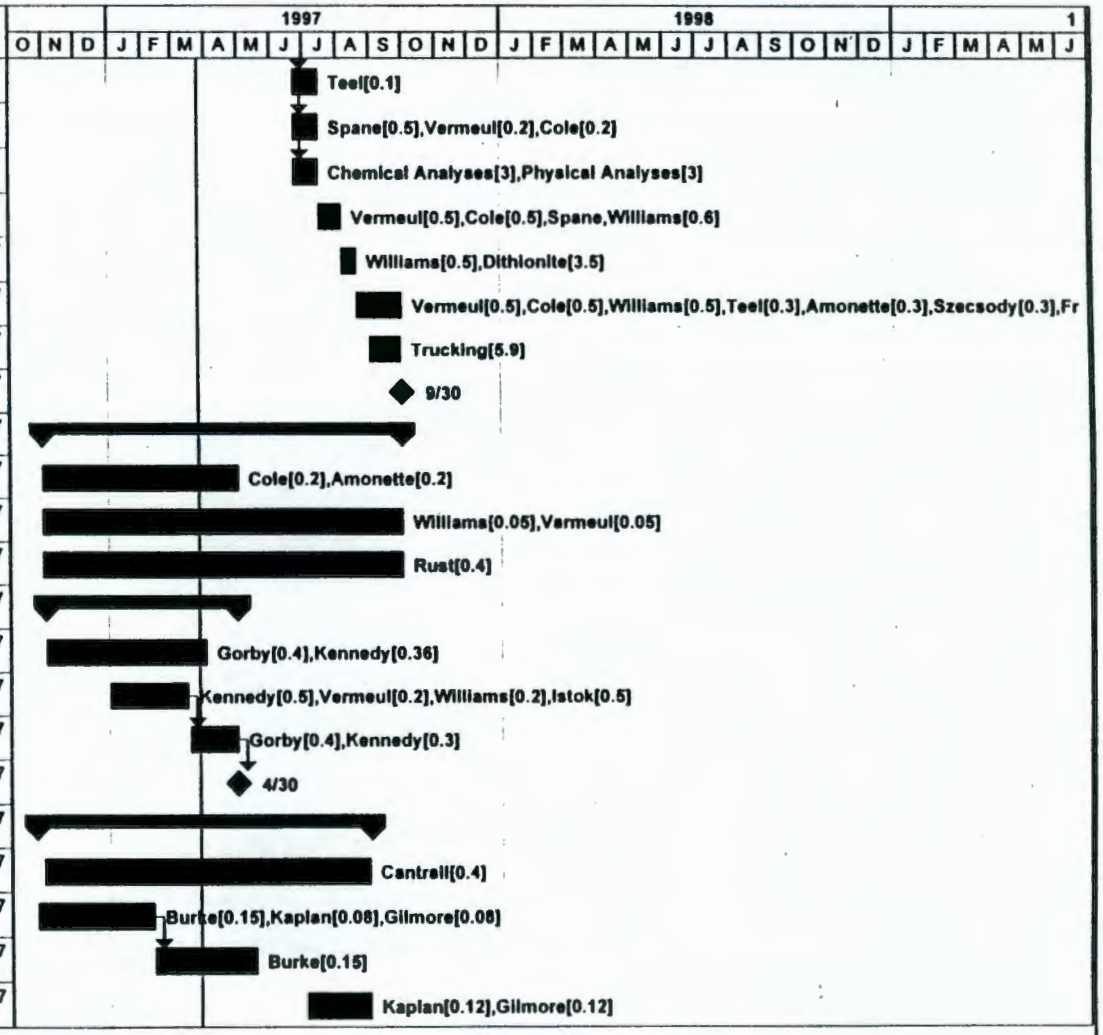
Table 16-1. ISRM Treatability Test Project Schedule (continued).

ID	Task Name	Start	Finish
23	Chromate A	Mon 6/23/97	Tue 7/15/97
24	Hydraulic t	Mon 6/23/97	Tue 7/15/97
25	Physical a	Mon 6/23/97	Tue 7/15/97
26	Tracer test	Wed 7/16/97	Tue 8/5/97
27	Purchase Dithi	Wed 8/6/97	Tue 8/19/97
28	Inject Dithionit	Wed 8/20/97	Wed 10/1/97
29	Purge Water S	Mon 9/1/97	Mon 9/29/97
30	Complete Dithi	Tue 9/30/97	Tue 9/30/97
31	Monitoring - 100H	Fri 11/1/96	Tue 9/30/97
32	Prepare Journal Arti	Fri 11/1/96	Wed 4/30/97
33	Well Monitoring	Fri 11/1/96	Tue 9/30/97
34	Maintenence	Fri 11/1/96	Tue 9/30/97
35	UMB Studies	Mon 11/4/96	Wed 4/30/97
36	UMB Experimen	Mon 11/4/96	Mon 3/31/97
37	Intermediate-Sc	Thu 1/2/97	Fri 3/14/97
38	Prepare UMB R	Mon 3/17/97	Tue 4/29/97
39	Deliver UMB Re	Wed 4/30/97	Wed 4/30/97
40	Iron Colloid Studies	Fri 10/25/96	Sun 8/31/97
41	Iron Colloid Exp	Fri 11/1/96	Fri 8/29/97
42	Column Experim	Fri 10/25/96	Mon 2/10/97
43	Natural Material	Mon 2/10/97	Thu 5/15/97
44	Prepare Iron Co	Tue 7/1/97	Fri 8/29/97



Project: Redox97
Date: Tue 3/25/97

Task | Progress | Milestone | Summary | Rolled Up Task | Rolled Up Milestone | Rolled Up Progress

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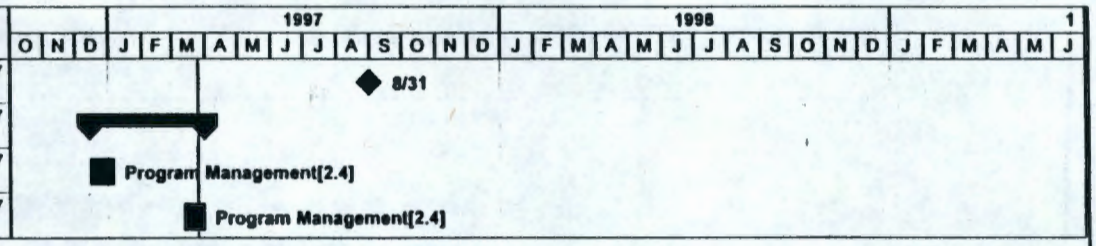
Table 16-1. ISRM Treatability Test Project Schedule (continued).

ID	Task Name	Start	Finish
45	Deliver Iron Coll	Sun 8/31/97	Sun 8/31/97
46	Program Management	Sun 12/15/96	Mon 3/31/97
47	First Half	Sun 12/15/96	Mon 1/6/97
48	Second Half	Wed 3/12/97	Mon 3/31/97



Project: Redox97
Date: Tue 3/25/97

Task | Progress | Milestone | Summary | Rolled Up Task | Rolled Up Milestone | Rolled Up Progress

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APPENDIX A

SAMPLING AND ANALYSIS PLAN

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APPENDIX A

SAMPLING AND ANALYSIS PLAN

A1.0 SCOPE OF WORK

The scope of work encompassed in this Sampling and Analysis Plan (SAP) includes the collection and analysis of groundwater and sediment samples from the saturated zone. Samples will be collected during the various stages of the ISRM treatability test at the 100-D/DR Area of the Hanford Site. The treatability test includes the following elements.

- Injection/Withdrawal and Monitoring Well Installation
- Background Sampling
- Tracer Injection/Withdrawal Test
- Barrier Emplacement
- Post-Emplacement Characterization
- Up/Downgradient Chromate Monitoring (ongoing)
- Performance Assessment Tracer Experiment
- Corehole Installation.

The logic and explanation of the various stages is discussed in the test plan.

This SAP covers sampling and analysis activities for the 100-D Area ISRM Treatability Study. This SAP consists of two main sections. Section 2.0 is the Field Sampling Plan (FSP) that details the requirements for collecting samples. Section 3.0 is the Quality Assurance Project Plan (QAPjP) that either provides or references procedures for making accurate measurements and obtaining representative, accurate, and precise analytical data from the sampling.

The characterization of the aquifer sediments during drilling is the subject of the Description *of Work Pre-Design Characterization in Support of the 100-D In Situ Redox Manipulation Treatability Test* (See Appendix D). The scope of work to be performed under that document includes pre-design characterization well drilling and sampling.

A2.0 FIELD SAMPLING PLAN

This FSP defines the sampling methodologies and strategies that will be used during each stage of the treatability test.

A2.1 SAMPLING OBJECTIVES

The objective of the sampling activities described in this FSP is to satisfy the data needs presented in Section A3.4 of the QAPjP. The data obtained will be used to evaluate the effectiveness of the ISRM technology at treating chromium-contaminated groundwater.

A2.2 GENERAL PROCEDURES

Field sampling will be conducted in accordance with the applicable Procedures for Ground-Water Investigations (PNL-MA-567). These procedures include the following:

Procedures for Ground-Water Investigations (PNL-MA-567)

AD-2	Ground-Water Sample Chain-of-Custody Procedure
AD-4	Sediment Sample Chain-of-Custody Procedure
AD-5	Ground-Water Sample Check-In Procedure
AD-6	Control Measures for Identification of Wells Requiring Purgewater Containment
AD-7	Control Measures for Identification of Samples Requiring Offsite Radioactive Shipping Documentation
GC-1	Ground-Water Sample Collection Procedure
SA-1	Sediment Sample Analysis/Sample Control Procedure
GC-11	Preparation of Documents and Sample Containers for Ground-Water Sample Collection
WL-1	Water-Level Measurement Procedure
DO-1	Collection and Documentation of Borehole Samples and Well Construction Data
AT-6	Aquifer Slug Injection and Withdrawal Test

Specific Procedures

NHFP-AT-07	Slug Interference Test
NHFP-AT-09	Tracer-Dilution and Tracer Drift/Pumpback Tests
NHFP-AT-10	Procedure for Conducting a Forced Gradient Tracer Test

A2.2.1 Sample Processing

Samples will be transported by staff to either the designated offsite laboratory or to the specified onsite laboratory personnel responsible for analysis. Unused sample material will be disposed of at the collection site or by the laboratory personnel according to laboratory procedures. All sample handling will be documented on chain-of-custody forms, per AD-2 (Ground-Water Sample Chain-of-Custody Procedure) or AD-4 (Sediment Sample Chain-of-Custody Procedure).

A2.3 SAMPLING STRATEGY/FREQUENCY

The sampling and analysis stages correspond to the data quality objective (DQO) activities presented in Section A3.4 of the QAPjP (Table A-3). For convenience of discussion, related activities have been grouped together.

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A2.3.1 Pre-design Characterization

As previously mentioned, sampling and analysis for the pre-design characterization wells (Activities A and B) is described in the corresponding description of work (DOW) included in Appendix D. Once these three activities are completed, the test barrier will be designed and the scope of work covered by this sampling and analysis plan will commence.

A2.3.2 Field Characterization and Site Preparation

The field characterization and site preparation task involves collecting background samples (Activity D); drilling the injection/withdrawal and monitoring wells (Activity C) as shown in the conceptual design in Figure 5-2 of the Treatability Test Plan (TTP); and performing the injection/withdrawal tracer test (Activity E).

Water quality testing is needed to establish a baseline before the barrier is installed. In addition, water and sediment samples may need to be collected during the drilling in Activity C to verify parameters collected during the pre-design characterization and analysis phase. The frequency of this sampling will be determined after the pre-design characterization (Activities A and B) and barrier design have been completed and will be documented in the drilling DOW for the barrier emplacement.

An injection/residence/withdrawal test will be conducted at the site with a nonreactive conservative tracer prior to the barrier emplacement. This test will determine the larger scale porosity of the aquifer, the amount of sodium dithionite required for injection, the amount of wastewater generated during the withdrawal, and the rates and durations needed for injection and withdrawal. The test will be conducted on the center injection/withdrawal well. Additional tracer tests may also be required on other injection/withdrawal wells based on observations in lithology.

A2.3.3 Permeable Treatment Barrier Emplacement

This task consists of emplacing the permeable treatment barrier (Activity F) through consecutive injection/residence/withdrawal stages in the injection wells shown in Figure 5-2 of the TTP.

For each of the injection wells, the injection and residence stages together last about 24 hr. The withdrawal stage will last a few days. During the operation at each injection well, the fluid in the feed tank, the monitoring wells, and overlapping injection wells will be collected and analyzed for dithionite concentrations. The frequency of this sampling is summarized in Table A-1. As with many of the other stages already discussed, sampling frequency cannot be determined until pre-design characterization data have been collected and analyzed.

Table A-1. Emplacement Sampling Frequency.

Analyte	Frequency
pH	To be determined based on well spacing and injection/withdrawal rates.
Dissolved Oxygen	
Eh	
Specific Conductivity	
Tracer	
Dithionite	
Chromate	Selected samples of injection stream, withdrawal stream, purgewater.
Nitrate	
Thiosulfate	
Sulfite	
Sulfate	
Trace Metals	

Finally, this task also includes analysis of withdrawn water from the ISRM test to determine how to treat or dispose of it.

A2.3.4 Barrier Performance Assessment and Monitoring

This task involves the evaluation of the permeable treatment barrier in its effectiveness in chromium remediation, impact on the water quality, and long-term capacity. The project stages included are post-emplacement characterization (Activity G), up/downgradient monitoring (ongoing) (Activity H), performance assessment tracer experiment (Activity I), and coreholes (Activity J).

After the barrier is emplaced, hydraulic testing (slug interference) is needed to determine if any detectable changes occurred to the hydraulic properties of the barrier/aquifer. The hydraulic testing will be per AT-6 or NHFP-AT-07 and will be performed on the first injection/withdrawal well. The water quality downgradient from the barrier will also be sampled, one sample per downgradient monitoring well.

As the main measure of the effectiveness of chromium remediation for the permeable treatment barrier, chromium concentrations will be monitored in the up and downgradient monitoring wells. Samples will be collected at an initial biweekly frequency, one sample per well. Sampling frequencies will be reduced to monthly or quarterly depending on groundwater travel time estimates and variations observed in the initial biweekly sampling.

Tracers will be added to the upgradient wells to determine the arrival of the upgradient water in the downgradient monitoring wells. The up/downgradient wells will be sampled to monitor the tracer; the frequency will be determined based on flow rate estimates (~weekly to monthly) until the tracer is below a minimum determined value.

Because of the slow estimated groundwater velocity in the region around the barrier, about 8 to 15 m/yr (25 to 50 ft/yr), some hydraulic control through the use of pumping or injection may be required to shorten the travel time from the upgradient to downgradient wells.

After the injection/residence/withdrawal operation has been completed at the injection wells, sediment samples will be collected by coreholes drilled within the barrier as shown in Figure 5-2 of

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APPENDIX A

SAMPLING AND ANALYSIS PLAN

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APPENDIX A

SAMPLING AND ANALYSIS PLAN

A1.0 SCOPE OF WORK

The scope of work encompassed in this Sampling and Analysis Plan (SAP) includes the collection and analysis of groundwater and sediment samples from the saturated zone. Samples will be collected during the various stages of the ISRM treatability test at the 100-D/DR Area of the Hanford Site. The treatability test includes the following elements.

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- Up/Downgradient Chromate Monitoring (ongoing)
- Performance Assessment Tracer Experiment
- Corehole Installation.

The logic and explanation of the various stages is discussed in the test plan.

This SAP covers sampling and analysis activities for the 100-D Area ISRM Treatability Study. This SAP consists of two main sections. Section 2.0 is the Field Sampling Plan (FSP) that details the requirements for collecting samples. Section 3.0 is the Quality Assurance Project Plan (QAPjP) that either provides or references procedures for making accurate measurements and obtaining representative, accurate, and precise analytical data from the sampling.

The characterization of the aquifer sediments during drilling is the subject of the Description *of Work Pre-Design Characterization in Support of the 100-D In Situ Redox Manipulation Treatability Test* (See Appendix D). The scope of work to be performed under that document includes pre-design characterization well drilling and sampling.

A2.0 FIELD SAMPLING PLAN

This FSP defines the sampling methodologies and strategies that will be used during each stage of the treatability test.

A2.1 SAMPLING OBJECTIVES

The objective of the sampling activities described in this FSP is to satisfy the data needs presented in Section A3.4 of the QAPjP. The data obtained will be used to evaluate the effectiveness of the ISRM technology at treating chromium-contaminated groundwater.

A2.2 GENERAL PROCEDURES

Field sampling will be conducted in accordance with the applicable Procedures for Ground-Water Investigations (PNL-MA-567). These procedures include the following:

Procedures for Ground-Water Investigations (PNL-MA-567)

AD-2	Ground-Water Sample Chain-of-Custody Procedure
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AD-5	Ground-Water Sample Check-In Procedure
AD-6	Control Measures for Identification of Wells Requiring Purgewater Containment
AD-7	Control Measures for Identification of Samples Requiring Offsite Radioactive Shipping Documentation
GC-1	Ground-Water Sample Collection Procedure
SA-1	Sediment Sample Analysis/Sample Control Procedure
GC-11	Preparation of Documents and Sample Containers for Ground-Water Sample Collection
WL-1	Water-Level Measurement Procedure
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Specific Procedures

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A2.2.1 Sample Processing

Samples will be transported by staff to either the designated offsite laboratory or to the specified onsite laboratory personnel responsible for analysis. Unused sample material will be disposed of at the collection site or by the laboratory personnel according to laboratory procedures. All sample handling will be documented on chain-of-custody forms, per AD-2 (Ground-Water Sample Chain-of-Custody Procedure) or AD-4 (Sediment Sample Chain-of-Custody Procedure).

A2.3 SAMPLING STRATEGY/FREQUENCY

The sampling and analysis stages correspond to the data quality objective (DQO) activities presented in Section A3.4 of the QAPjP (Table A-3). For convenience of discussion, related activities have been grouped together.

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A2.3.1 Pre-design Characterization

As previously mentioned, sampling and analysis for the pre-design characterization wells (Activities A and B) is described in the corresponding description of work (DOW) included in Appendix D. Once these three activities are completed, the test barrier will be designed and the scope of work covered by this sampling and analysis plan will commence.

A2.3.2 Field Characterization and Site Preparation

The field characterization and site preparation task involves collecting background samples (Activity D); drilling the injection/withdrawal and monitoring wells (Activity C) as shown in the conceptual design in Figure 5-2 of the Treatability Test Plan (TTP); and performing the injection/withdrawal tracer test (Activity E).

Water quality testing is needed to establish a baseline before the barrier is installed. In addition, water and sediment samples may need to be collected during the drilling in Activity C to verify parameters collected during the pre-design characterization and analysis phase. The frequency of this sampling will be determined after the pre-design characterization (Activities A and B) and barrier design have been completed and will be documented in the drilling DOW for the barrier emplacement.

An injection/residence/withdrawal test will be conducted at the site with a nonreactive conservative tracer prior to the barrier emplacement. This test will determine the larger scale porosity of the aquifer, the amount of sodium dithionite required for injection, the amount of wastewater generated during the withdrawal, and the rates and durations needed for injection and withdrawal. The test will be conducted on the center injection/withdrawal well. Additional tracer tests may also be required on other injection/withdrawal wells based on observations in lithology.

A2.3.3 Permeable Treatment Barrier Emplacement

This task consists of emplacing the permeable treatment barrier (Activity F) through consecutive injection/residence/withdrawal stages in the injection wells shown in Figure 5-2 of the TTP.

For each of the injection wells, the injection and residence stages together last about 24 hr. The withdrawal stage will last a few days. During the operation at each injection well, the fluid in the feed tank, the monitoring wells, and overlapping injection wells will be collected and analyzed for dithionite concentrations. The frequency of this sampling is summarized in Table A-1. As with many of the other stages already discussed, sampling frequency cannot be determined until pre-design characterization data have been collected and analyzed.

Table A-1. Emplacement Sampling Frequency.

Analyte	Frequency
pH	To be determined based on well spacing and injection/withdrawal rates.
Dissolved Oxygen	
Eh	
Specific Conductivity	
Tracer	
Dithionite	
Chromate	Selected samples of injection stream, withdrawal stream, purgewater.
Nitrate	
Thiosulfate	
Sulfite	
Sulfate	
Trace Metals	

Finally, this task also includes analysis of withdrawn water from the ISRM test to determine how to treat or dispose of it.

A2.3.4 Barrier Performance Assessment and Monitoring

This task involves the evaluation of the permeable treatment barrier in its effectiveness in chromium remediation, impact on the water quality, and long-term capacity. The project stages included are post-emplacement characterization (Activity G), up/downgradient monitoring (ongoing) (Activity H), performance assessment tracer experiment (Activity I), and coreholes (Activity J).

After the barrier is emplaced, hydraulic testing (slug interference) is needed to determine if any detectable changes occurred to the hydraulic properties of the barrier/aquifer. The hydraulic testing will be per AT-6 or NHFP-AT-07 and will be performed on the first injection/withdrawal well. The water quality downgradient from the barrier will also be sampled, one sample per downgradient monitoring well.

As the main measure of the effectiveness of chromium remediation for the permeable treatment barrier, chromium concentrations will be monitored in the up and downgradient monitoring wells. Samples will be collected at an initial biweekly frequency, one sample per well. Sampling frequencies will be reduced to monthly or quarterly depending on groundwater travel time estimates and variations observed in the initial biweekly sampling.

Tracers will be added to the upgradient wells to determine the arrival of the upgradient water in the downgradient monitoring wells. The up/downgradient wells will be sampled to monitor the tracer; the frequency will be determined based on flow rate estimates (~weekly to monthly) until the tracer is below a minimum determined value.

Because of the slow estimated groundwater velocity in the region around the barrier, about 8 to 15 m/yr (25 to 50 ft/yr), some hydraulic control through the use of pumping or injection may be required to shorten the travel time from the upgradient to downgradient wells.

After the injection/residence/withdrawal operation has been completed at the injection wells, sediment samples will be collected by coreholes drilled within the barrier as shown in Figure 5-2 of

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the TTP. This sediment will be analyzed to determine the amount of iron reduction that occurred within the barrier. This will be accomplished by both iron analysis and column studies of the reoxygenation of the sediment to determine the treatment capacity of the reduced sediment within the barrier. The number of coreholes to be drilled will be determined from pre-design characterization data. Groundwater may need to be sampled from the coreholes to compare to pre-design characterization data. The frequency of groundwater sample collection will be determined from pre-design characterization data. Although direct measurements of reduction capacity and estimates of lifetime will be based on the analysis of the corehole sediments, long-term monitoring of the wells at the site will be conducted to detect any loss of treatment capacity and to assess environmental impacts.

A2.4 SAMPLE COLLECTION PROCEDURES

Sediment and groundwater sample collection procedures will be consistent throughout all of the stages of the project unless otherwise specified.

A2.4.1 Sediment Sampling

Sediment samples shall be collected for analyses presented for Activity J, Coreholes, in Table 3-2. The samples shall be collected in Lexan liners; the priority for liner capping of reactable iron, treatment capacity, porosity and bulk density, and physical property samples is as follows:

1. Reactable iron and treatment capacity sample Lexan liner capping
2. Physical property sample liner capping.

The individual steps for each of these activities are described in the following sections.

Reactable Iron and Treatment Capacity Sample Liner Capping

Capping the sample liner for reactable iron analysis is conducted after the liner has been retrieved, as follows:

- Cap both ends of the liner with vinyl end caps
- Write the date and time of sampling, the well number and depth, and the sampler's initials on the Lexan liner and mark on or attach a label to the liner: (1) "CHEM"; and (2) an arrow pointing in the up direction.

Porosity and Bulk Density Sampling

The liner designated for porosity and bulk density analyses must be completely full of sediment. This will ensure that the sediment structure is not destroyed during transport and that sediment samples are representative of the particle size fraction present in the sampled interval. Cap and label as above, except that the liner is labeled "PHYS" instead of "CHEM".

A2.4.1.1 Sample Preservation Procedures. Preservation procedures for reactable iron samples, particle size samples, and porosity and bulk density samples are described below.

Reactable Iron and Treatment Capacity Sediment Samples

The liner designated for reactable iron or treatment capacity characterization will be sealed with end caps and will be refrigerated and kept in an oxygen-free environment (plastic bag filled with argon gas) until delivery to the laboratory to maintain iron valence.

Porosity/Bulk Density and Particle Size Samples

Porosity/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 remains intact, the Lexan 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 holding time limit for the porosity and bulk density samples is 90 days.

A2.4.2 Groundwater Sampling

Groundwater samples will be collected according to GC-1.

A2.4.2.1 Sample Collection and Preservation Procedures. Tests will be conducted during the tracer studies to determine the purge volume required to obtain a representative sample. If this volume cannot be adequately determined, three casing volumes shall be purged from the well prior to sampling. Purgewater will be stored in the modular tank that will be used for temporary storage of the groundwater extracted as part of the emplacement phase of the treatability test. Purgewater management will be in accordance with the Waste Control Plan (Appendix E) for drilling activities and in accordance with Section 4.4 (Waste and Wastewater Management) of this TTP for other activities. During emplacement, the fluid in the feed tank will be monitored for dithionite concentrations.

A2.4.2.2 Quality Control Samples. Quality control requirements are listed in the Quality Assurance Project Plan (Section A3.0).

A2.4.2.3 Sample Disposal. Samples sent off of the Hanford Site will be disposed of as specified by the contract with the laboratory. Sampled material that remains on the Hanford Site will be disposed of according to the waste control plan.

A3.0 QUALITY ASSURANCE PROJECT PLAN

A3.1 PROJECT DESCRIPTION/OBJECTIVE

This Quality Assurance Project Plan applies to sampling and data-gathering activities in support of the In Situ Redox Treatability Test in the 100-HR-3 Operable Unit, 100-D Area. Data resulting from this test will be utilized to evaluate the suitability of the ISRM technology for remediation of the chromium-contaminated groundwater in the 100-D/DR Area of the Hanford Site.

The purpose of this QAPjP is to specify the overall procedures and controls for performing sampling and data gathering activities with the level of quality control commensurate with the cost, schedule and risks associated with this project. All staff working within the scope of PNNL responsibilities will be trained to this QA Plan and will meet its requirements during performance of the work.

A3.1.1 Client

U.S. Department of Energy

A3.1.2 Authorizing Document

DOE, EM-50 (Metals and Radionuclides Remediation), TTP number RL-3-7-SS-52.

A3.1.3 QA Requirements Specification(s)

Impact Level III activities shall comply with the applicable requirements of PNL-MA-70 for the work being performed. This QAPjP also identifies client QA requirements and any imposed exclusions or limitations to PNNL procedure requirements. If other quality-related activities are later performed, the appropriate PNL-MA-70 requirements and procedures shall be applied, unless specifically excluded.

A3.1.4 QA Program/Organization

The QA program described here was developed to address the U. S. Environmental Protection Agency's (EPA) QAMS-005/80, Interim Guidelines for Preparing Quality Assurance Project Plans. PNNL's current Quality Assurance Program is documented in the Quality Assurance manual, PNL-MA-70. It is based on ASME NQA-1-1989, Quality Assurance Program Requirements for Nuclear Facilities and meets the majority of the requirements of DOE 5700.6C.

A3.1.5 Impact Level

The Impact Level for this project has been designated Impact Level III.

A3.1.6 Change Control (Scope, Schedule, Budget)

Requests for changes in project scope, schedule or budget from that in the Test Plan (other than changes in the sampling site, frequency, or parameters) must be documented and receive approval from the client.

A3.2 PROJECT DESCRIPTION

Pacific Northwest National Laboratory (PNNL), the developer of the ISRM technology, has conducted experiments to test the viability of the ISRM technology from bench-scale to field-scale testing. The ISRM Project began in fiscal year (FY) 1992 through DOE's Office of Health and Environmental Research - Subsurface Science Program. As part of this ISRM project, laboratory

proof-of-principle abiotic and biotic studies, conceptual design reports, and preliminary planning documents were prepared (Fruchter et al. 1995). The potential for a remediation technology based on in situ manipulation of subsurface redox conditions has been established through theory and proof-of-principle laboratory experiments. However, attempts to control redox potential in an aquifer must overcome various scale-up complications arising from the interaction between contaminants, reducing agents, groundwater, and the natural variability of the subsurface. In FY 1994, a site at 100-H Area was selected for field-scale experiments of the ISRM technology. The laboratory and design studies as well as the FY 1994 and 1995 field tests were funded through DOE's Office of Technology Development's In Situ Remediation Integrated Program.

Results of these experiments will be used to design this full-scale field demonstration. This treatability test will demonstrate the ISRM technology on a pilot scale in the 100-D Area. Reduction of ferric iron will be accomplished by injecting and withdrawing aqueous sodium dithionite into the aquifer. Hexavalent chromium in the groundwater moving through this zone will be reduced to the less soluble and less toxic trivalent form of chromium.

A3.3 PROJECT ORGANIZATION AND RESPONSIBILITIES

The responsibilities of key PNNL and ERC personnel are summarized in Table A-2.

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TABLE A-2. KEY PROJECT PERSONNEL

PERSONNEL	RESPONSIBILITIES
PNNL Project Manager (JS Fruchter)	Ensures that all project objectives are accomplished in a timely manner and within the program budget. Assigns qualified staff to the project. Ensures the quality of the work done on the project and maintains direct communication with the client.
PNNL Technical Lead (CR Cole, MD Williams)	Works directly with the Project Manager and Staff. Provides technical oversight for the project.
PNNL Task Leaders (VR Vermeul, SS Teel)	Provide planning and management assistance to the Project Manager by developing planning documents, directing day-to-day activities to accomplish the project objectives, and coordinate tasks, personnel and schedules. Manage the budget, investigate suspect results, and review records. Contribute relevant task information to the final technical memoranda.
PNNL Project Staff	Perform testing and sampling activities in accordance with methods identified in the planning documents. Works under supervision of the Task Leaders.
BHI Groundwater Environmental Lead (AJ Knepp)	Coordinates BHI technology transfer activities. Works with the PNNL Project Manager to ensure that all project objectives are accomplished. Coordinates all BHI activities.
BHI Subcontract Technical Representative (STR)/Field Superintendent (RC Havenor)	Provides direction and oversight to the drilling subcontractor. Coordinates drilling support activities. Monitors and maintains safe and efficient working conditions. Interfaces directly with on-site PNNL staff during drilling.

A3.4 QA OBJECTIVES FOR MEASUREMENTS

The data collected for this project will be used to evaluate the suitability of the ISRM technology for remediation of the chromium-contaminated groundwater in the 100-D/DR Area of the Hanford Site. It is critical that sampling activities are well planned and conducted according to procedures to ensure representativeness and comparability as well as a level of precision and accuracy to be expected from field activities. To assure the quality of the data, quality control specifications for measuring precision and accuracy will be given to the laboratory in the Statement of Work .

A3.4.1 Data Quality

The characteristics used to define data quality are accuracy, precision, completeness, comparability, and representativeness. These terms are defined in the following sections. The definitions for accuracy and precision terms are those contained in Appendix A of QAMS-005/80, Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans.

Analytical requirements (detection limit/range/accuracy) are shown in Table A-3. Representativeness and comparability of data are ensured through procedures and well planned sampling practices and activities and, as defined in Appendix A of QAMS-005/80, will be addressed, as appropriate, in deliverable reports.

A3.4.1.1 Accuracy

Accuracy is a measure of the error between reported test results and the true sample concentration. Insomuch as true sample concentrations are not known, accuracy is usually inferred from recovery data as determined by sample spiking.

For the laboratory metals analyses, the laboratories will analyze samples spiked with a known concentration of a reference standard to assess laboratory accuracy. Perfect accuracy is 100 percent recovery; acceptable accuracies are ±25% recovery. Matrix spikes will be analyzed at a frequency recommended by the analytical method or Laboratory QA manual.

A.3.4.1.2 Precision

Precision is a measure of the variability of the data when more than one measurement is made on the same sample. Variability is commonly attributable to sampling activities and/or chemical analysis. For duplicate measurements, precision can be expressed as the relative percent difference (RPD). Analysis of field duplicate samples measures the precision of sampling procedures. Analysis of laboratory duplicate samples will serve to measure the precision of laboratory procedures. Laboratory duplicates will be analyzed at a frequency recommended by the analytical method and/or laboratory QA Plan. The objectives for precision are 20% RPD. The frequency at which field duplicate samples should be collected is 10 percent.

A.3.4.1.3 Completeness

Completeness is defined as the total number of samples taken for which acceptable analytical data are generated divided by the total number of samples analyzed and multiplied by 100. An overall completeness goal for this project has been set at 95 percent.

A.3.4.1.4 Comparability

Comparability expresses the confidence that one data set can be compared to another. Comparability of the data will be maintained by using established procedures in both the sampling activities and the analytical methods used.

A.3.4.1.5 Representativeness

Representativeness is a measure of how closely the measured results reflect the actual concentration or distribution of the chemical constituent in the matrix sampled.

Representativeness is accomplished by choosing sampling procedures that will produce results that depict as accurately and precisely as possible the matrix and conditions being measured; by developing protocols for storage, preservation, and transportation that preserve the representativeness of the collected samples; and by using documentation methods that assure that protocols have been followed and that samples are properly identified so that their integrity is maintained.

A.3.4.1.6 Detection Limit

The detection limit refers to the reporting detection limit that the lab will report as per the Laboratory Statement of Work (SOW). Detection limits are shown in Table A-3.

A3.5 SAMPLING AND LABORATORY PROCEDURES

A list of procedures that will be used for this work is shown in Table A-3 and A-4. These procedures include field procedures, sampling procedures, and laboratory procedures.

A3.5.1 Sampling Procedures

All samples shall be collected in accordance with the requirements contained in the Sampling and Analysis Plan (Section A.1.0 and A.2.0).

A.3.5.2 Analytical Chemistry Procedures

The analytical laboratories performing analyses will use procedures noted in Table A-3. The analytical chemistry lab manager will be responsible for all chemistry analyses. Requirements for the analysis will be documented in a Statement of Work (SOW) to the lab. The analyses will be distributed as listed below. Changes to this list shall be approved by the Project Manager prior to submittal to the laboratory for analysis.

A3.6 SAMPLE CUSTODY AND FIELD/LAB DOCUMENTATION

All of the samples shall be handled in such a manner to ensure sample integrity. The sample containers shall be sealed to minimize moisture loss and prevent possible contamination, and shall be kept cold, but not frozen, until delivered to the place of testing.

A3.6.1 Sample Chain-of-Custody

The chain-of-custody of samples from the field to the analytical labs shall be controlled in accordance with **PNL-MA-567, AD-2: Ground-Water Sample Chain of Custody and Field Record Form Procedure.**

A3.6.2 Field Record Forms

Field Record Forms, Field Notebooks, or the Geologists Log will be used to document field sampling activities performed by PNNL staff. Field Record Forms are used for groundwater sampling, conductivity, pH and water level measurements in accordance with the **PNL-MA-567, AD-2: Ground-Water Sample Chain of Custody and Field Record Form Procedure**. Field Log Books or Geologists Logs shall be used to document collection of the sediment samples.

If Laboratory Record Books (LRB) are used to document other activities they shall be used in accordance with the requirements contained in **PNL-MA-68, Section 6.2, Laboratory Record Books**.

Only black ink shall be used to record information on data forms and the LRBs. Pencil drafts may be used provided that record originals are prepared by photocopying or through transcription onto another form. If the penciled documents are transcribed onto another form, the original pencil document shall also be kept as a record.

A3.6.3 Corrections to Documentation

If an error is made on any field or laboratory documentation, an individual may correct the error by drawing a single line through the error and entering the correct information. The error shall not be obliterated. All non-editorial corrections shall be initialed and dated.

A.3.7 CALIBRATION PROCEDURES AND FREQUENCY

All measuring and test equipment (M&TE) must be controlled in accordance with PNL-MA-70 Administrative Procedure **PAP-70-1201, Calibration Control System.** All M&TE used on this project shall be traceable to the data collected and shall be calibrated before use.

A3.7.1 Field Instrument Calibration

Field instruments used in obtaining water quality data (i.e. pH, temperature, and conductivity) must be calibrated daily before use in accordance with manufacurer's specifications; such calibration shall be documented on standardized data forms.

A3.7.2 Analytical Chemistry Calibration

Calibration methods for all chemical analytical processes shall be addressed in each specific procedure. As a minimum, calibrations should include:

- standards that are traceable to nationally recognized standard organization(s)
- standards that are within their expiration date
- using standard concentrations that bracket the expected concentration of the sample(s)

All laboratory equipment shall either be calibrated or performance checked with traceable standards (bulletted above) as applicable, prior to work being performed for this project.

A3.8 DATA MANAGEMENT AND REPORTING

Analytical results shall be entered into the project database and verified against the hard copy spreadsheet or data report.

In addition to original deliverables from the laboratories, a computer database shall be maintained to store results of field measurements, laboratory analyses, and groundwater level measurements. Field measurements will be recorded on standardized data forms.

A3.8.1 Sample Tracking

Sample tracking procedures shall used to indicate whether analytical samples collected are contained, transported, and analyzed according to methods and holding times specified. The sample tracking shall verify that analyses requested for each sample listed on the chain-of-custody were performed by the analytical laboratories. Printouts shall be generated for any outstanding results or discrepancies.

A3.8.2 Data Entry

Data shall be entered into the database manually or by direct download of laboratory supplied electronic data. Regardless of the method of data entry, data entry quality control shall be maintained through several types of data checking. Data checking is carried out prior to merging the temporary input file with the master database file. This checking system shall involve direct comparison of hardcopy listings of the temporary input database to the hardcopy laboratory or field reports. If corrections are required, they will be written directly on the printout. Once the correction is made, a revised printout will be placed with the original to document the change. Notations will be made of the date and the initials of the reviewer. After the corrections are completed, the log will be dated and initialed. Following correction of any inconsistencies in either the data file or the laboratory reports, the temporary input file is merged to a proxy master file. This proxy file is used as a daily working file, and backups of it as well as the master file are maintained.

A3.8.3 Process for Handling Suspect or Unacceptable Data

When the initial data review identifies suspect data, that data must be investigated to establish whether it reflects true conditions or an error. The investigation shall be documented. If the data value is determined to be in error, the source of the error must be investigated, the correct value established if possible, and the erroneous value replaced with the correct value. If the investigation concludes that the data are suspect (possibly in error) but a correct value cannot be determined, the data must be flagged to indicate its suspect status.

A3.9 INTERNAL QUALITY CONTROL CHECKS

<u>CHEMISTRY ANALYSIS</u>

Matrix Spikes - All matrix spike recoveries which are outside the established DQOs shall be noted in the narrative and flagged on the final data report. In addition, the number of results which exceed the range per batch shall be noted to determine if the problem affects the sample data for that batch and to determine any other appropriate corrective action

Surrogates - For parameters where one surrogate is used, all samples with recoveries outside the established limits (see Table 6.2) need to be re-extracted and re-analyzed. When multiple surrogates are used, and more than one is outside of these limits, re-extraction and re-analysis of that sample is required. If after re-analysis, the same recoveries are outside

the limits, the problem will be considered a matrix effect and a third re-extraction and re-analysis is not required.

Replicates - All samples associated with replicates (matrix spike duplicates and triplicates) that are outside the established control limits will be noted in the narrative and flagged in the final data report. In addition, the number of results which exceed the range per batch shall be noted to determine if the problem affects the sample data for that batch and to determine any other appropriate corrective action.

SRMs - SRM values exceeding the PD range from the certified value should be noted in the narrative and flagged in the final data report. In addition, the number of results which exceed the range per batch shall be noted to determine if the problem affects the sample data for that batch and to determine any other appropriate corrective action.

Method Blanks - Any blank values detected above the established criteria should be noted in the narrative and the corresponding data should be flagged as blank contaminated. In addition, the number of results which exceed the range per batch shall be noted to determine if the problem affects the sample data for that batch and to determine any other appropriate corrective action.

Equipment Blanks - Frequency for equipment blank collection will be based on the number of samples collected each day. Equipment blanks will be collected at a frequency of 5 percent or once per day when 10 or more samples are collected per day. When less than 10 samples are collected per day, this batch of samples will be submitted with the samples and equipment blank collected on the following day. Field duplicate samples will be collected at least once per day for each sample parameter (and for each media type, if more than one sampled per day. Laboratory method blanks, used to assess the level of laboratory background contamination, will be analyzed at a frequency specified by the analytical method.

A3.10 ASSESSMENTS

Project management will determine if areas of the project should be assessed to ensure that key requirements are being met. These assessments, if performed, will be in accordance with **QP-07, Management Self-Assessments**, with the exception that a memo may be utilized as a reporting format. The results of assessments shall be made available to project and line management as well as to key individuals contacted.

A3.11 SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY, COMPARABILITY AND COMPLETENESS

Because of the nature of environmental measurements, it is frequently difficult or impossible to know the "true" value of the measured parameter. The accuracy of the measured value must instead be inferred through the use of QC samples of known composition. This project uses this method to verify that the data quality objectives (DQOs) have been met.

The task leader will verify that data precision, accuracy, comparability, and completeness are reviewed and within the DQOs. Results of this review will be included in the final report.

A3.12 CORRECTIVE ACTION

Results outside the established criteria in Table A-2 shall be brought to the attention of the Task Leader and the Project Manager who shall determine and document the appropriate corrective action. These actions may include, but are not limited to, review of data and calculations, flagging of suspect data or re-analyses of individual or entire batches of samples.

The need for corrective action may be identified by the technical staff during the course of their work. Each individual performing field, laboratory, or data processing activities will be responsible for notifying the appropriate supervisory personnel of any circumstance that could affect the quality or integrity of the data.

Unplanned deviations from procedural, contractual, or regulatory requirements must be documented by completing a Deficiency Report (DR) in accordance with PNL-MA-70 Administrative Procedure **PAP-70-1502, Deficiency Reports (DRs)**. The DR must identify the requirement deviated from, the cause of the deviation, whether any results were effected, and corrective action needed to remedy the immediate problem and to prevent recurrence.

Planned deviations, documented (including justification) and approved by the Project Manager or Task Leader in advance, do not constitute a deficiency as defined in PAP-70-1502 and do not require development of a DR. Deviations typically result from unforeseen circumstances and must be documented. Deviations are different from deficiencies and will be documented in a field notebook or geologists log.

A3.13 QUALITY ASSURANCE REPORTS TO MANAGEMENT

Significant problems (e.g., problems affecting the quality of the work) uncovered by project personnel must be reported to line management immediately for resolution. Significant problems involving data quality or sample integrity must be thoroughly documented. Line management must be included on the distribution of all audit and surveillance reports. Significant problems encountered in day-to-day operations must be reported to line management immediately by the Project Manager.

QA assessment results will be documented and reported to the Project Manager and Task Leaders when assessments are performed.

A3.14 RECORDS

Records shall be indexed and subsequently maintained in accordance with **PAP-70-1701, Records System**. All project records shall be made available for storage after project completion and/or after client approval of the final report. The retention period for storage shall be specified on the Records Inventory/Disposition Schedule (RIDS). Records will not be turned over to the client unless specifically requested.

A3.15 PROCUREMENT CONTROL

Procurement of items and subcontracted services are governed by PNL-MA-70 Administrative Procedure **PAP-70-401, Purchase Requisitions**.

Samples submitted to analytical labs shall be accompanied with, as a minimum, directions for the following: 1) chain-of-custody; 2) analysis turnaround time; 3) QC requirements; 4) methods; and

5) notification of PNNL staff when Data Quality Objective (DQO) requirements are not met. Corrective action for DQO exceedences shall be coordinated with PNNL and analytical staff and shall follow the guidance of section 13.0 of this QAPjP.

A3.16 STAFF TRAINING

Staff performing activities affecting quality shall have documented training for the applicable administrative procedures and standard operating procedures, the Sampling and Analysis Plan and this QAPjP.

Training shall be documented in accordance with **PNL-MA-4, PNNL Training and Qualification Manual**, either through the issuance of training assignments for read/study training or through briefings given by the Quality Engineer, Program Manager or Task Leaders, or others, as appropriate.

Table A-3. Analytical Requirements for the ISRM Treatability Test. (10 Sheets)

A - Pre-Design Characterization			
Aqueous Sampling and Analysis			
Parameter	Analysis Method		Detection Limit / Range / Accuracy
Chromate	diphenylcarbazide method Hach 8023[1], SM-3500-Cr-D[2], EPA 7196[4]		0.005 - 0.6 ppm
pH	pH Electrode Hach 8156[1], SM-4500-H[2]		± 0.1
Alkalinity	Sulfuric Acid / Titration Hach 8203[1]		10 - 4000 ppm
Dissolved Oxygen	Membrane Electrode SM-4500-O G[2]		±1 % (air sat)
Conductivity	Electrode Hach 8160[1], SM-2510[2]		± 1 µS/cm
Nitrate	Colorimetric indicator test strip FSP-1-12[1], DOE MS-310[3]		0.7 - 50 ppm
	Cd reduction, diazotization	Hach 8192[1]	0.01 - 0.40 ppm
		Hach 8171[1]	0.1 - 4.5 ppm
		Hach 8039[1]	1.0 - 30.0 ppm
Sulfate	$BaSO_4$ method Hach 8051[1]		5 - 70 ppm
Sediment Sampling and Analysis[a]			
Parameter	Analysis Method		Detection Limit / Range / Accuracy
Specific Gravity Bulk Density/Porosity	ASTM[5] or other Standard Method		n/a
Grain Size Distribution	Sieve, ASTM[5] or other Standard Method		n/a
Lithologic Description	Field Geologist, DO-1 [7]		n/a
Accessible Iron and Reaction Rate Analysis	Dithionite Treatment (PNNL Laboratory-Specific Procedure)[6]		n/a
Hydraulic Sampling and Analysis			
Parameter	Analysis Method		Detection Limit / Range / Accuracy
Hydraulic Head	Standardized Steel Tape or Water-Level Indicator, WL-1[7]		0.003 m (0.01 ft)

Notes: a) Sediment samples from one well must be sealed in an argon-gas filled bags and temporarily stored in coolers for preservation of iron valence within the samples. These samples will be transferred to anaerobic chambers for analysis.

Table A-3. Analytical Requirements for the ISRM Treatability Test. (10 Sheets)

B - Initial Hydraulic Test		
Aqueous Sampling and Analysis		
Parameter	Analysis Method	Detection Limit / Range / Accuracy
n/a		
Sediment Sampling and Analysis		
Parameter	Analysis Method	Detection Limit / Range / Accuracy
n/a		
Hydraulic Sampling and Analysis		
Parameter	Analysis Method	Detection Limit / Range / Accuracy
Hydraulic Conductivity	Slug Interference and/or Constant Rate Discharge Test, AT-6 and/or NHFP-AT-07 [7]	n/a
Specific Yield	Constant Rate Discharge Test, AT-6 and/or NHFP-AT-07 [7]	n/a
Specific Storage	Slug Interference and/or Constant Rate Discharge Test, AT-6 and/or NHFP-AT-07 [7]	n/a
Maximum Production Rate	Step Drawdown Test, AT-6 [7]	n/a
Hydraulic Head	Water-Level Indicator or Pressure Transducer, manufacturer's instructions	n/a

Table A-3. Analytical Requirements for the ISRM Treatability Test. (10 Sheets)

C - Injection/Withdrawal and Monitoring Well Installation			
Aqueous Sampling and Analysis			
Parameter	Analysis Method		Detection Limit / Range / Accuracy
Chromate	diphenylcarbazide method Hach 8023[1], SM-3500-Cr-D[2], EPA 7196[4]		0.005 - 0.6 ppm
pH	pH Electrode Hach 8156[1], SM-4500-H[2]		± 0.1
Alkalinity	Sulfuric Acid / Titration Hach 8203[1]		10 - 4000 ppm
Dissolved Oxygen	Membrane Electrode SM-4500-O G[2]		±1 % (air sat)
Conductivity	Electrode Hach 8160[1], SM-2510[2]		± 1 µS/cm
Nitrate	Colorimetric indicator test strip FSP-1-12[1], DOE MS-310[3]		0.7 - 50 ppm
	Cd reduction, diazotization	Hach 8192[1]	0.01 - 0.40 ppm
		Hach 8171[1]	0.1 - 4.5 ppm
		Hach 8039[1]	1.0 - 30.0 ppm
Sulfate	$BaSO_4$ method Hach 8051[1]		5 - 70 ppm
Sediment Sampling and Analysis			
Parameter	Analysis Method		Detection Limit / Range / Accuracy
Specific Gravity Bulk Density/Porosity	ASTM[5] or other Standard Method		n/a
Grain Size Distribution	Sieve, ASTM[5] or other Standard Method		n/a
Lithologic Description	Field Geologist, DO-1[7]		n/a
Accessible Iron and Reaction Rate Analysis	Dithionite Treatment Method (PNNL Laboratory-Specific Procedure)[6]		n/a
Hydraulic Sampling and Analysis			
Parameter	Analysis Method		Detection Limit / Range / Accuracy
Hydraulic Head	Standardized Steel Tape or Water-Level Indicator, WL-1[7]		0.003 m (0.01 ft)

Table A-3. Analytical Requirements for the ISRM Treatability Test. (10 Sheets)

D - Background		
Aqueous Sampling and Analysis		
Parameter	Analysis Method	Detection Limit / Range / Accuracy
Chromate	diphenylcarbazide method Hach 8023[1], SM-3500-Cr-D[2], EPA 7196[4]	0.005 - 0.6 ppm
pH	pH Electrode Hach 8156[1], SM-4500-H[2]	± 0.1
Alkalinity	Sulfuric Acid / Titration Hach 8203[1]	10 - 4000 ppm
Dissolved Oxygen	Membrane Electrode SM-4500-O G[2]	±1 % (air sat)
Conductivity	Electrode Hach 8160[1], SM-2510[2]	± 1 µS/cm
ICP Metals (filtered) Na, Mg, Si, K, Ca, Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Sb, Ba, Pb, U	SW-846, 6010	75% - 125%
Anions (Cl, SO4, PO4, NO2, NO3)	EPA 300.0	75% - 125%
NO2-NO3	EPA 353.1	75% - 125%
SO3	EPA 377.1	75% - 125%
Sulfide	SW-846 9030	75% - 125%
Ammonia	EPA 350.1	75% - 125%
Sediment Sampling and Analysis		
Parameter	Analysis Method	Detection Limit / Range / Accuracy
none		
Hydraulic Sampling and Analysis		
Parameter	Analysis Method	Detection Limit / Range / Accuracy
Hydraulic Head	Standardized Steel Tape or Water-Level Indicator, WL-1[7]	0.003 m (0.01 ft)

Table A-3. Analytical Requirements for the ISRM Treatability Test. (10 Sheets)

E- Tracer Injection/Withdrawal Test		
Aqueous Sampling and Analysis		
Parameter	Analysis Method	Detection Limit / Range / Accuracy
Tracer (bromide)	Ion Specific Electrode	75% - 125%
Sediment Sampling and Analysis		
Parameter	Analysis Method	Detection Limit / Range / Accuracy
n/a		
Hydraulic Sampling and Analysis		
Parameter	Analysis Method	Detection Limit / Range / Accuracy
Hydraulic Head	Pressure Transducer, manufacturer's instructions	n/a
Injection/Withdrawal Rate	Flow Meter, manufacturer's instructions	n/a
Hydraulic Conductivity, Specific Yield, and Specific Storage	Constant Rate Discharge Test, AT-6 and/or NHFP-AT-07 [7]	n/a
Maximum Production Rate	Step Drawdown Test, AT-6 [7]	n/a

Table A-3. Analytical Requirements for the ISRM Treatability Test. (10 Sheets)

F - Emplacement			
Aqueous Sampling and Analysis[a]			
Parameter	Analysis Method		Detection Limit / Range / Accuracy
pH	pH Electrode Hach 8156[1], SM-4500-H[2]		± 0.1
Alkalinity	Sulfuric Acid / Titration Hach 8203[1]		10 - 4000 ppm
Dissolved Oxygen	Membrane Electrode SM-4500-O G[2]		±1 % (air sat)
Conductivity	Electrode Hach 8160[1], SM-2510[2]		± 1 µS/cm
Tracer	Ion Specific Electrode		75% - 125%
Dithionite	UV/Vis or HPLC		0.0001 M
Chromate	diphenylcarbazide method Hach 8023[1], SM-3500-Cr-D[2], EPA 7196[4]		0.005 - 0.6 ppm
Nitrate	Colorimetric indicator test strip FSP-1-12[1], DOE MS-310[3]		0.7 - 50 ppm
	Cd reduction, diazotization	Hach 8192[1]	0.01 - 0.40 ppm
		Hach 8171[1]	0.1 - 4.5 ppm
		Hach 8039[1]	1.0 - 30.0 ppm
Thiosulfate	Ion Chromatography		75% - 125%
Sulfite	iodate-iodide method Hach 8071[1]		1 ppm
Sulfate	$BaSO_4$ method Hach 8051[1]		5 - 70 ppm
Trace Metals (filtered) Na, Mg, Si, K, Ca, Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Sb, Ba, Pb, U	SW-846 6010		75% - 125%
Sediment Sampling and Analysis			
Parameter	Analysis Method		Detection Limit / Range / Accuracy
none			
Hydraulic Sampling and Analysis			
Parameter	Analysis Method		Detection Limit / Range / Accuracy
Inj/Wdrwl Rate	Flow Meter		n/a
Hydraulic Head	Pressure transducer		n/a

Notes: a) Aqueous sampling/analysis will be conducted on the injection solution, monitoring wells, withdrawal water, and purgewater storage.

Table A-3. Analytical Requirements for the ISRM Treatability Test. (10 Sheets)

G - Post-Emplacement Characterization		
Aqueous Sampling and Analysis		
Parameter	Analysis Method	Detection Limit / Range / Accuracy
Chromate	diphenylcarbazide method Hach 8023[1], SM-3500-Cr-D[2], EPA 7196[4]	0.005 - 0.6 ppm
pH	pH Electrode Hach 8156[1], SM-4500-H[2]	± 0.1
Alkalinity	Sulfuric Acid / Titration Hach 8203[1]	10 - 4000 ppm
Dissolved Oxygen	Membrane Electrode SM-4500-O G[2]	±1 % (air sat)
Conductivity	Electrode Hach 8160[1], SM-2510[2]	± 1 µS/cm
Thiosulfate	Ion Chromatography	75% - 125%
ICP Metals (filtered) Na, Mg, Si, K, Ca, Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Sb, Ba, Pb, U	SW-846 6010	75% - 125%
Anions (Cl, SO4, NO2, NO3)	EPA 300.0	75% - 125%
NO2-NO3	353.1	75% - 125%
SO3	EPA 377.1	75% - 125%
Sulfide	9030	75% - 125%
Ammonia	EPA 350.1	75% - 125%
Sediment Sampling and Analysis		
Parameter	Analysis Method	Detection Limit / Range / Accuracy
none		
Hydraulic Sampling and Analysis[a]		
Parameter	Analysis Method	Detection Limit / Range / Accuracy
Hydraulic Head	Pressure Transducer	n/a
Withdrawal Rate	Flow Meter	n/a
Hydraulic Conductivity, and Specific Storage	Slug Interference Test and/or Constant Rate Discharge Test, AT-6 and/or NHFP-AT-07 [7]	n/a

Notes: a)The Hydraulic tests will be conducted in the central injection/withdrawal well.

Table A-3. Analytical Requirements for the ISRM Treatability Test. (10 Sheets)

H- Up/Downgradient Chromate Monitoring			
Aqueous Sampling and Analysis			
Parameter	Analysis Method		Detection Limit / Range / Accuracy
Chromate	diphenylcarbazide method Hach 8023[1], SM-3500-Cr-D[2], EPA 7196[4]		0.005 - 0.6 ppm
pH	pH Electrode Hach 8156[1], SM-4500-H[2]		± 0.1
Alkalinity	Sulfuric Acid / Titration Hach 8203[1]		10 - 4000 ppm
Dissolved Oxygen	Membrane Electrode SM-4500-O G[2]		±1 % (air sat)
Conductivity	Electrode Hach 8160[1], SM-2510[2]		± 1 µS/cm
Nitrate	Colorimetric indicator test strip FSP-1-12[1], DOE MS-310[3]		0.7 - 50 ppm
	Cd reduction, diazotization	Hach 8192[1]	0.01 - 0.40 ppm
		Hach 8171[1]	0.1 - 4.5 ppm
		Hach 8039[1]	1.0 - 30.0 ppm
Sulfate	$BaSO_4$ method Hach 8051[1]		5 - 70 ppm
Sediment Sampling and Analysis			
Parameter	Analysis Method		Detection Limit / Range / Accuracy
none			
Hydraulic Sampling and Analysis			
Parameter	Analysis Method		Detection Limit / Range / Accuracy
Hydraulic Head	Standardized Steel Tape or Water-Level Indicator, WL-1[7]		0.003 m (0.01 ft)

Table A-3. Analytical Requirements for the ISRM Treatability Test. (10 Sheets)

I - Performance Assessment Tracer Experiment			
Aqueous Sampling and Analysis			
Parameter	Analysis Method		Detection Limit / Range / Accuracy
Tracer (species TBD)	Field method (ion specific probe)		
Chromate	diphenylcarbazide method Hach 8023[1], SM-3500-Cr-D[2], EPA 7196[4]		0.005 - 0.6 ppm
pH	pH Electrode Hach 8156[1], SM-4500-H[2]		± 0.1
Alkalinity	Sulfuric Acid / Titration Hach 8203[1]		10 - 4000 ppm
Dissolved Oxygen	Membrane Electrode SM-4500-O G[2]		±1 % (air sat)
Conductivity	Electrode Hach 8160[1], SM-2510[2]		± 1 µS/cm
Nitrate	Colorimetric indicator test strip FSP-1-12[1], DOE MS-310[3]		0.7 - 50 ppm
	Cd reduction, diazotization	Hach 8192[1]	0.01 - 0.40 ppm
		Hach 8171[1]	0.1 - 4.5 ppm
		Hach 8039[1]	1.0 - 30.0 ppm
Sulfate	$BaSO_4$ method Hach 8051[1]		5 - 70 ppm
Sediment Sampling and Analysis			
Parameter	Analysis Method		Detection Limit / Range / Accuracy
none			
Hydraulic Sampling and Analysis			
Parameter	Analysis Method		Detection Limit / Range / Accuracy
Tracer Test	NHFP-AT-09 and/or NHFP-AT-10[7]		n/a
Hydraulic Head	Standardized Steel Tape or Water-Level Indicator, EIP 7.1[8]0.003 m (0.01 ft)		0.003 m (0.01 ft)

Table A-3. Analytical Requirements for the ISRM Treatability Test. (10 Sheets)

J - Coreholes

Aqueous Sampling and Analysis

Parameter	Analysis Method		Detection Limit / Range / Accuracy
Chromate	diphenylcarbazide method Hach 8023[1], SM-3500-Cr-D[2], EPA 7196[4]		0.005 - 0.6 ppm
pH	pH Electrode Hach 8156[1], SM-4500-H[2]		± 0.1
Alkalinity	Sulfuric Acid / Titration Hach 8203[1]		10 - 4000 ppm
Dissolved Oxygen	Membrane Electrode SM-4500-O G[2]		±1 % (air sat)
Conductivity	Electrode Hach 8160[1], SM-2510[2]		± 1 µS/cm
Nitrate	Colorimetric indicator test strip FSP-1-12[1], DOE MS-310[3]		0.7 - 50 ppm
	Cd reduction, diazotization	Hach 8192[1]	0.01 - 0.40 ppm
		Hach 8171[1]	0.1 - 4.5 ppm
		Hach 8039[1]	1.0 - 30.0 ppm
Sulfate	$BaSO_4$ method Hach 8051[1]		5 - 70 ppm

Sediment Sampling and Analysis[a]

Parameter	Analysis Method	Detection Limit / Range / Accuracy
Specific Gravity Bulk Density/Porosity	ASTM[5] or other Standard Method	n/a
Grain Size Distribution	Sieve, ASTM[5] or other Standard Method	n/a
Lithologic Description	Field Geologist, DO-1[7]	n/a
Accessible ferric Iron Analysis	Dithionite Treatment Method	n/a
Treatment Capacity (pore volumes of oxygenated water and chromate)	Bench-Scale Chromate Treatment Experiments (batch or column)	n/a

Hydraulic Sampling and Analysis

Parameter	Analysis Method	Detection Limit / Range / Accuracy
none		

Notes: a) All sediment samples must be sealed in an argon-gas filled bags and temporarily stored in coolers for preservation of iron valence within the samples. They will be transferred to anaerobic chambers for analysis.

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[1]Hach (1992); **Water Analysis Handbook, 2nd Edition**, Hach Company, Loveland, CO, 1992.

[2]APHA/AWWA/WPCF (1989); **Standard Methods for the Examination of Water and Wastewater, 17th Edn**; American Public Health Association, Washington, DC, 1989.

[3]Goheen, S.C. et al (editors) (1994); **DOE Methods for Evaluating Environmental and Waste Management Samples**; U.S. Department of Energy, DOE/EM-0089T, Rev 2.

[4]EPA (1989); **Test Methods for Evaluating Solid Waste**; SW-846, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.

[5]ASTM; **Annual Book of ASTM Standards**, American Society for Testing and Materials, Philadelphia, Pennsylvania.

[6]Material will be treated by PNNL with dithionite in an anaerobic glovebox. Dithionite concentrations in the sediment/dithionite mixture will be measured periodically (~ hourly). The reaction rate of the reduction of ferric iron by dithionite is significantly faster than the disproportionation and degradation rates; therefore, the rate of decrease in dithionite concentration is much less after all the accessible ferric iron is reduced. A plot of the dithionite concentration vs elapsed time is constructed for use in determining when all the accessible ferric iron is reduced.

[7] EIP 7.0, **Procedures for Ground-Water Investigations (PNL-MA-567)**

WL-1 Water-Level Measurement Procedure
DO-1 Collection and Documentation of Borehole Samples and Well Construction Data
AT-6 Aquifer Slug Injection and Withdrawal Test

[8] **Specific Procedures**

NHFP-AT-07 Slug Interference Test
NHFP-AT-09 Tracer-Dilution and Tracer Drift/Punpback Tests
NHFP-AT-10 Procedure for Conducting a Forced Gradient Tracer Test

Table A-4 Field Procedures

Procedures for Ground-Water Investigations (PNL-MA-567)

AD-2	Ground-Water Sample Chain-of-Custody Procedure
AD-4	Sediment Sample Chain-of-Custody Procedure
AD-5	Ground-Water Sample Check-In Procedure
AD-6	Control Measures for Identification of Wells Requiring Purgewater Containment
AD-7	Control Measures for Identification of Samples Requiring Offsite Radioactive Shipping Documentation
GC-1	Ground-Water Sample Collection Procedure
SA-1	Sediment Sample Analysis/Sample Control Procedure
GC-11	Preparation of Documents and Sample Containers for Ground-Water Sample Collection
FA-1	Temperature Measurement Procedure
FA-2	Calibration of Conductivity Meter and Measurement of Field Conductivity
FA-3	Calibration of pH meter and Measurement of Field pH
FA-4	Calibration of Turbidimeter and Measurement of Field Turbidity
WL-1	Water-Level Measurement Procedure
DO-1	Collection and Documentation of Borehole Samples and Well Construction Data
AT-6	Aquifer Slug Injection and Withdrawal Test

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APPENDIX B
CULTURAL AND ECOLOGICAL DOCUMENTATION

Cultural and Ecological Reviews were conducted in the vicinity of the proposed ISRM treatability test (Attachments B-1 and B-2) (Note: Hot Spot Well #1 is Well 199-D4-1). These reviews were conducted for the initial installation of the monitoring well 199-D4-1. No cultural or ecological resources would be threatened by the activities.

Additional Cultural, Ecologic and Biologic Reviews were performed in February-March 1997 to cover the entire area for the ISRM Test. The Cultural Resources Review is included in Attachment B-3, the Ecological Review is included in Attachment B-4, and the Biologic Review is included in Attachment B-5.

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ATTACHMENT B-1
CULTURAL RESOURCES REVIEW - 100-HR-3 GROUNDWATER MONITORING WELLS AT 100-D AREA (HCRC# 96-100-012B)

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Environmental Restoration Contractor **ERC Team**

Interoffice Memorandum

Job No. 22192
Written Response Required? NO
Closes CCN: N/A
OU: N/A
TSD: N/A
ERA: N/A
Subject Code: 6500

TO: R. C. Havenor, X1-85

DATE: October 3, 1996

COPIES: See Below

FROM: Darci D. Teel, Manager
Natural Resources & Risk Assessment
H0-02/372-9633

SUBJECT: **CULTURAL RESOURCES REVIEW - MONITORING WELLS AT 100-D (HCRC #96-100-012B**

In response to your request of October 2, 1996, a Cultural Resource Review was conducted for the 100-HR-3 Interim Remedial Action project. The scope of this project involves the installation of two monitoring wells at 100-D (Attachment 1). The Hanford Cultural Resources Management Plan identifies this project as a Class IV undertaking: New Construction in a Disturbed High Sensitivity Area.

A records and literature review was conducted for this project by Darby C. Stapp on October 3, 1996. A site visit was made on October 3, 1996. No cultural resources are recorded within or immediately adjacent to the project area. Hot Spot Well #1 is located in an area that has been covered extensively with gravel. No original ground surface could be observed at this location. Hot Spot Well #2 is located in an area that has also been graveled, but to a lesser extent. Some original ground surface was observed in this area. Given the disturbed nature of the two well locations and the absence of known cultural resources, and the minimal disturbance that will be created by the construction, this project can proceed as planned; no additional cultural resource work is needed.

Although highly unlikely, cultural materials could exist in the project area, therefore all workers must be directed to watch for cultural material (e.g., bone, stone tools) during all work activities. If any cultural materials are encountered as work proceeds, work in the vicinity of the discovery must stop until a Cultural Resources Specialist has been notified, the significance of the find is assessed, the appropriate Tribes are notified, and, if necessary, arrangements have been made for mitigation of the find. In the event of any discoveries, please contact Thomas E. Marceau at 372-9289.

If any changes occur relative to work scope or areas to be impacted, it is important that you contact the Cultural Resources staff for additional review/action that might be required. Please use the HCRC# 96-100-048 for any further correspondence concerning this project.

A copy of this memo will be formally transmitted by the ERC Manager of Projects to Dee W. Lloyd, Manager, Cultural Resources Program, A5-15, DOE-RL, as official documentaion at a later date.

Author Signature: Darby C. Stapp
Cultural Resources Coordinator

Approval Signature: Thomas E. Marceau
Cultural Resources Supervisor

Copies
N.A. Cadoret K6-75
K.A. Gano H0-02
A.J. Knepp H4-80
T.E. Marceau H0-02
W.L. Pamplin H0-18
D.C. Stapp H9-03
BHI Document Control H0-09

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ATTACHMENT B-2
ECOLOGICAL REVIEW FOR 100-HR-3 PIEZOMETER WELLS NEAR 100-D (96-ER-036)

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Environmental Restoration Contractor **ERC Team**

Interoffice Memorandum

Job No. 22192
Written Response Required? NO
Closes CCN: N/A
OU: N/A
TSD: N/A
ERA: N/A
Subject Code 8240

TO: R. C. Havenor X1-85

DATE: October 7, 1996

COPIES: K. A. Gano H0-02
C. J. Kemp H0-02
A. J. Knepp H4-80
T. E. Marceau H0-02
W. L. Pamplin H0-18
D. C. Stapp H9-03
S. G. Weiss H9-03
DDT: Letterbook H0-02
BHI Document Control H0-09

FROM: K A Gano for
D. D. Teel, Manager
Natural Resources & Risk Assessment
H0-02/372-9633

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SUBJECT: **ECOLOGICAL REVIEW OF TWO WELL SITES AT 100-D AREA (96-ER-036)**

This memo is in response to your request for an Ecological Review of two proposed well sites in the 100-HR-3 Operable Unit. One site is in the northeast corner of 100-D Area on the bluff near the 181-D Pumphouse. The other site is directly south approximately 400 meters, just off the paved road and directly east of the existing meteorology tower.

These two sites were surveyed by Natural Resources on October 4, 1996. The first site near the pumphouse is located on highly disturbed ground consisting of coarse gravels and sand. The small amount of vegetation present at this site consists of weedy species such as Russian thistle. The site near the tower is on a coarse sandy soil and contains cheatgrass, sand dropseed, yarrow, gray rabbitbrush, hoary aster, and a small amount of diffuse knapweed. Neither of these two sites support any plant or animal species of concern and no impacts to ecological resources will occur from construction of well pads at these locations.

If there are any major changes in the scope of activities that could result in any disturbance to soils or habitats outside the description of this project, please contact Ken Gano on 372-9316 and refer to the Ecological Review number given in the subject line.

KAG:dds

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Environmental Restoration Contractor **ERC Team**

Interoffice Memorandum

Job No. 22192
Written Response Required? NO
Closes CCN: N/A
OU: 100-DR-1
TSD: N/A
ERA: N/A
Subject Code: 6500

TO: Randall C. Havenor X1-85

DATE: February 11, 1997

COPIES: N. A. Cadoret K6-75
K. A. Gano H0-02
T. E. Marceau H0-02
A. J. Knepp H4-80
J. E. Rugg X5-53
J. J. Sharpe H9-03
BHI Document Control H4-79

FROM: Darci D. Teel, Manager
Natural Resources & Risk Assessment
H0-02/372-9633

SUBJECT: **CULTURAL RESOURCES REVIEW - 100-D AREA REDOX MANIPULATION TEST (PNNL), (HCRC # 96-100-012c).**

In response to your request of January 24, 1997, a Cultural Resources Review was conducted for the 100-D Area Redox Manipulation Test (PNNL). The project will involve leveling previously disturbed surface and installing up to 12 groundwater injection and monitoring wells (Figures 1 and 2). Four layout options for the well field are under consideration. Three of these options are immediately adjacent to the existing 199-D4-1 monitoring well (Figures 3-5); the last is approximately 250 feet southeast of this well (Figure 6). Each configuration requires an area approximately 75 feet by 150 feet. In order to create a suitable working surface, the high points in the previously disturbed area will be leveled by grading. This could include grading up to 12 inches in depth in some locations. Each well is to be drilled using a rotary air drilling system; all well holes will have a diameter of eight inches. The Hanford Cultural Resources Management Plan identifies this project as a Class IV undertaking: New Construction in a Disturbed High-Sensitivity Area. Our review indicates that the project may proceed as planned.

A records and literature review was conducted for this project on January 27, 1997, by James J. Sharpe, Cultural Resource Specialist. His review indicated that surface areas (i.e., access, well pad, laydown area, and a buffer zone) associated with the installation of Well 199-D4-1 (previously named Hot Spot Well #1) were inspected by ERC Cultural Resources staff on October 3, 1996. No cultural resources were observed within or adjacent to the project area which had been covered with clean gravel. This inspection noted that "no original ground surface could be observed" (HCRC# 96-100-012b).

Additional review indicates that previous surface and subsurface disturbances have occurred from 18 to 36 inches within this area. These historic disturbances have removed and/or altered the fine sediments which may have contained cultural material such that physical integrity has been lost. The *Soil Survey Hanford Project in Benton County Washington* describes the soil type for the project location as Ephrata Stony Loam. This soil type is described as "containing many large hummocky ridges made up of debris released from the melting ice of glaciers. Areas between hummocks contain many boulders several feet in diameter." Ephrata Sandy Loam and Burbank Loamy Sand are also associated and included in the soil matrix (BNWL-243).

Due to the extent of previous surface disturbance at the project location, and the rotary air drilling technique to be utilized, monitoring by ERC Cultural Resources staff will not be required. However, since Tribal representatives may elect to monitor this drilling, please contact Thomas E. Marceau (372-9289) one week prior to the beginning of scheduled drilling operations so that notification may be forwarded to the Tribes.

Although no cultural materials are expected to be impacted by this project, all workers must be directed to watch for cultural material (e.g., bone, stone tools) during all work activities. If any cultural materials are encountered during the construction project, work in the vicinity of the discovery must stop until a Cultural Resource Specialist has been notified, the significance of the find assessed, appropriate Tribes notified, and if necessary, arrangements made for mitigation of the find. In the event of any discoveries, please contact Mr. Marceau.

If any changes occur relative to work scope or areas to be impacted, it is imperative that you contact the Cultural Resources staff for additional review/action that might be required. Please use HCRL# 96-100-012c for any further correspondence concerning this project.

Please ensure that a copy of this memo is formally transmitted by the ERC Manager of Projects to Dee W. Lloyd, Manager, Cultural Resources Program, A5-15, DOE/RL, as official documentation upon receipt by your office. Please copy Mr. Marceau on this letter of transmittal.

Author Signature: James J. Sharpe
James J. Sharpe
Cultural Resources Specialist

Approval Signature: Thomas E. Marceau
Thomas E. Marceau
Cultural Resources Supervisor

References:

BNWL-243, 1966, *Soil Survey Hanford Project in Benton County Washington*. Pacific Northwest Laboratory, Richland, Washington.

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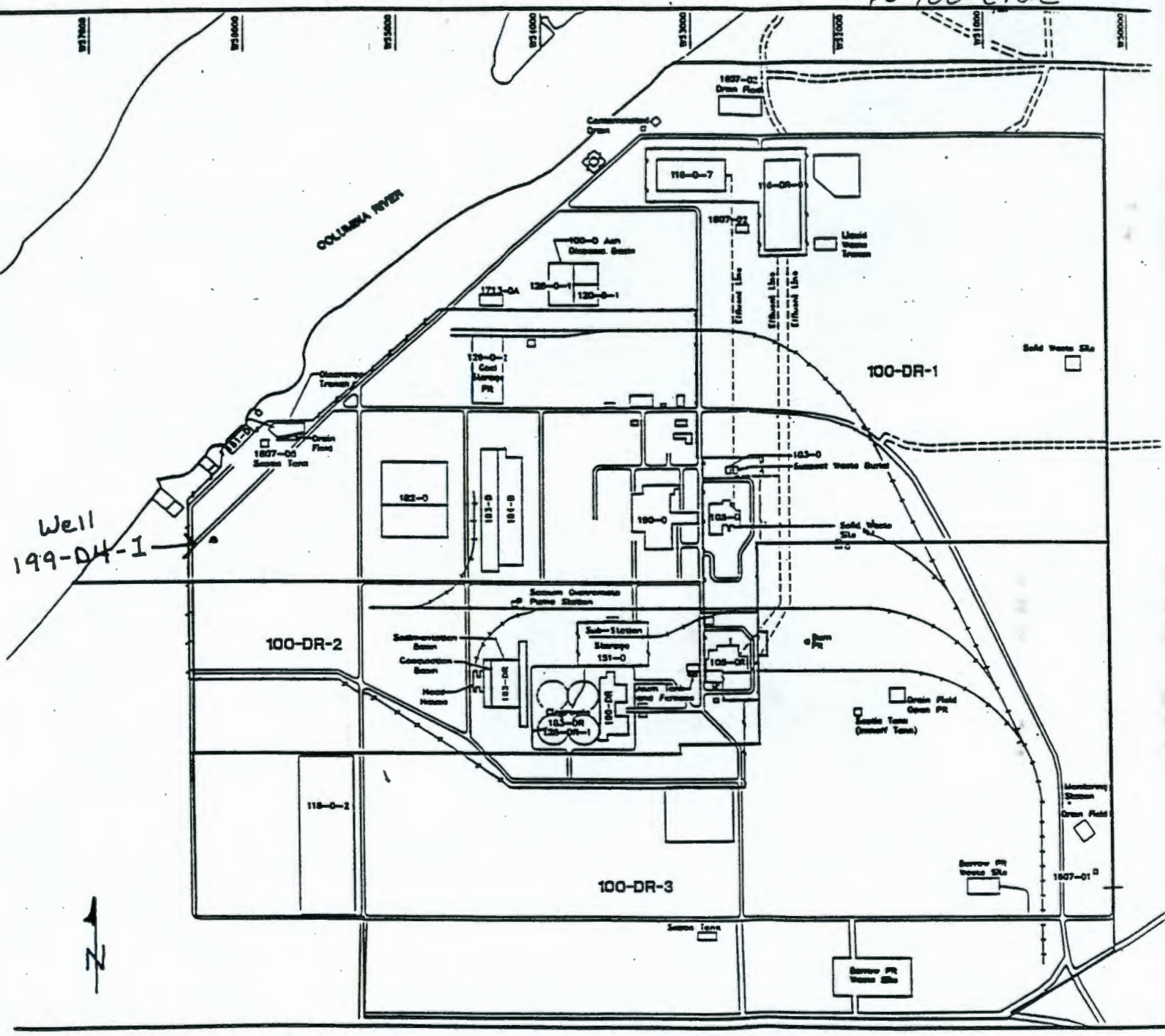
96-100-012C



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ok 2-13

Figure 1. Locations of 100-D Hot Spot Wells

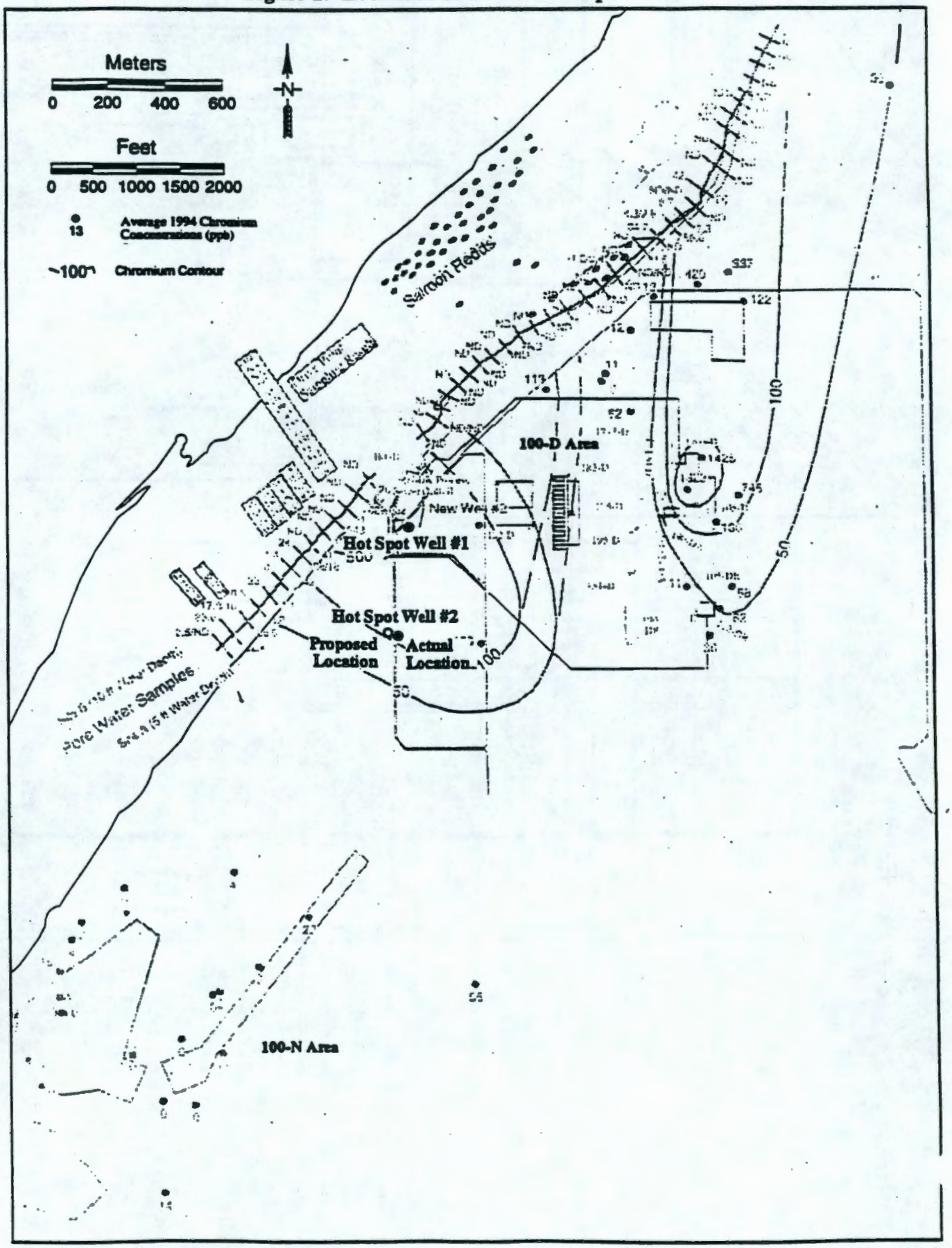
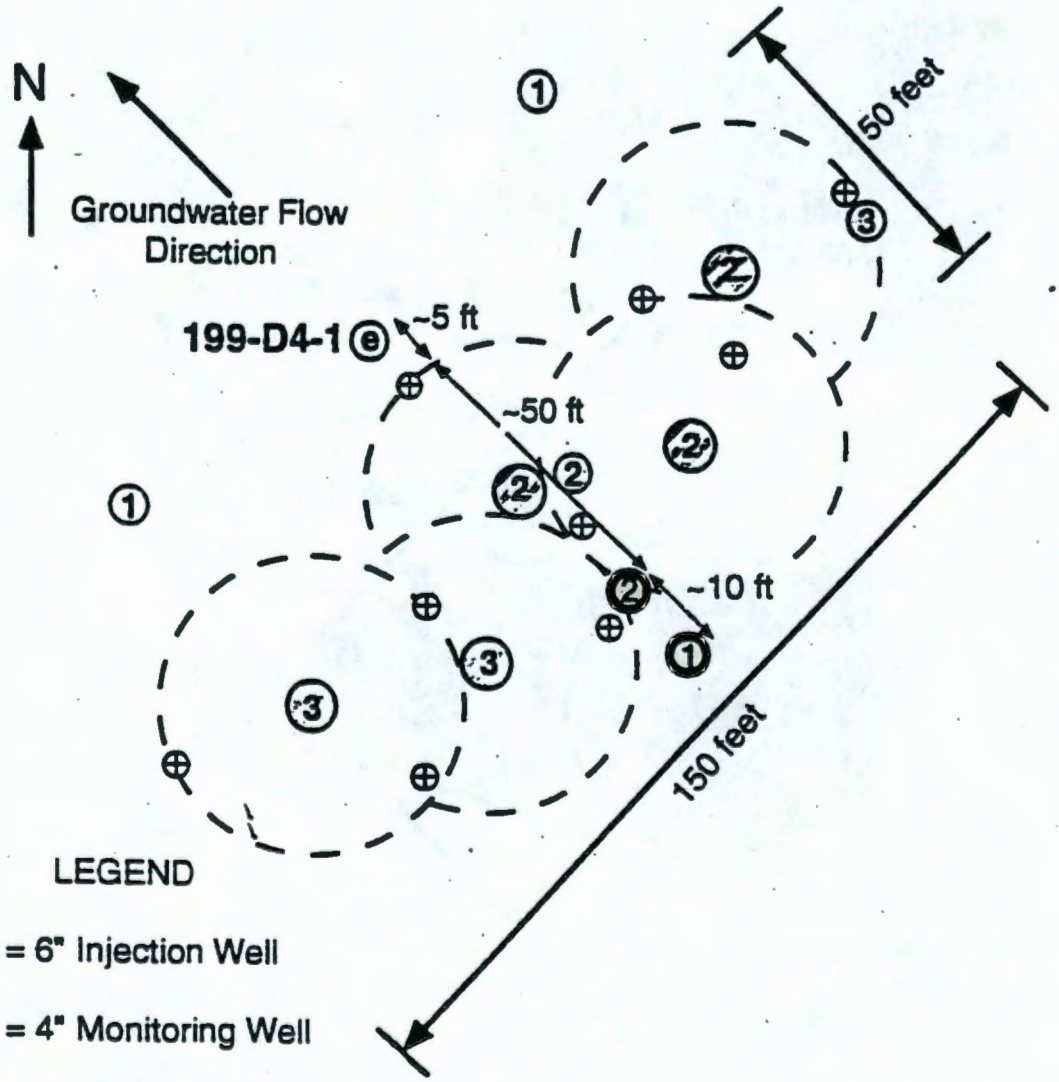


Figure 2.



LEGEND

= 6" Injection Well

= 4" Monitoring Well

= 4" Multi-level Monitoring Well

= Corehole

= Reduced Zone

1 2 3 4 Number indicates phase of drilling

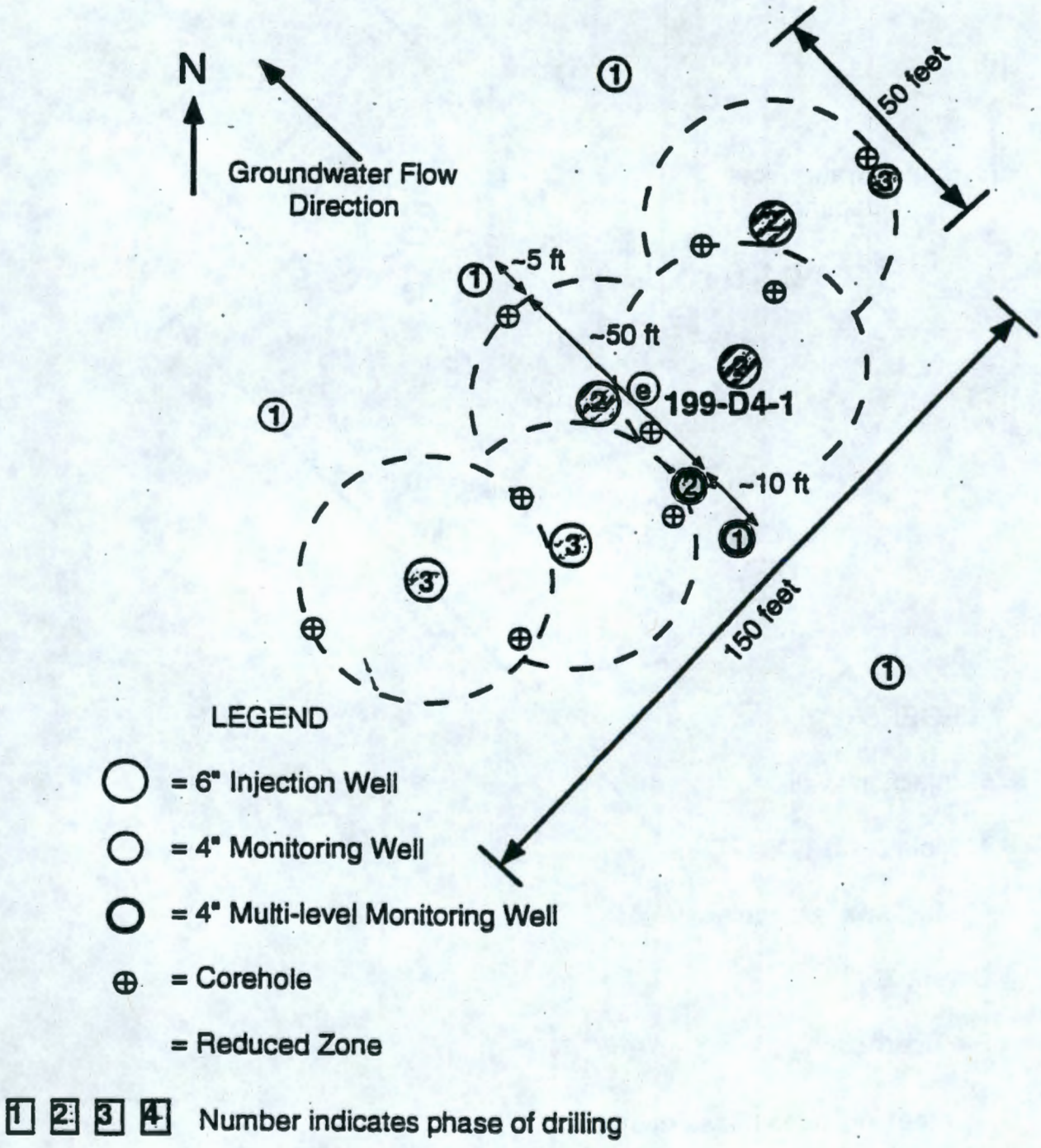
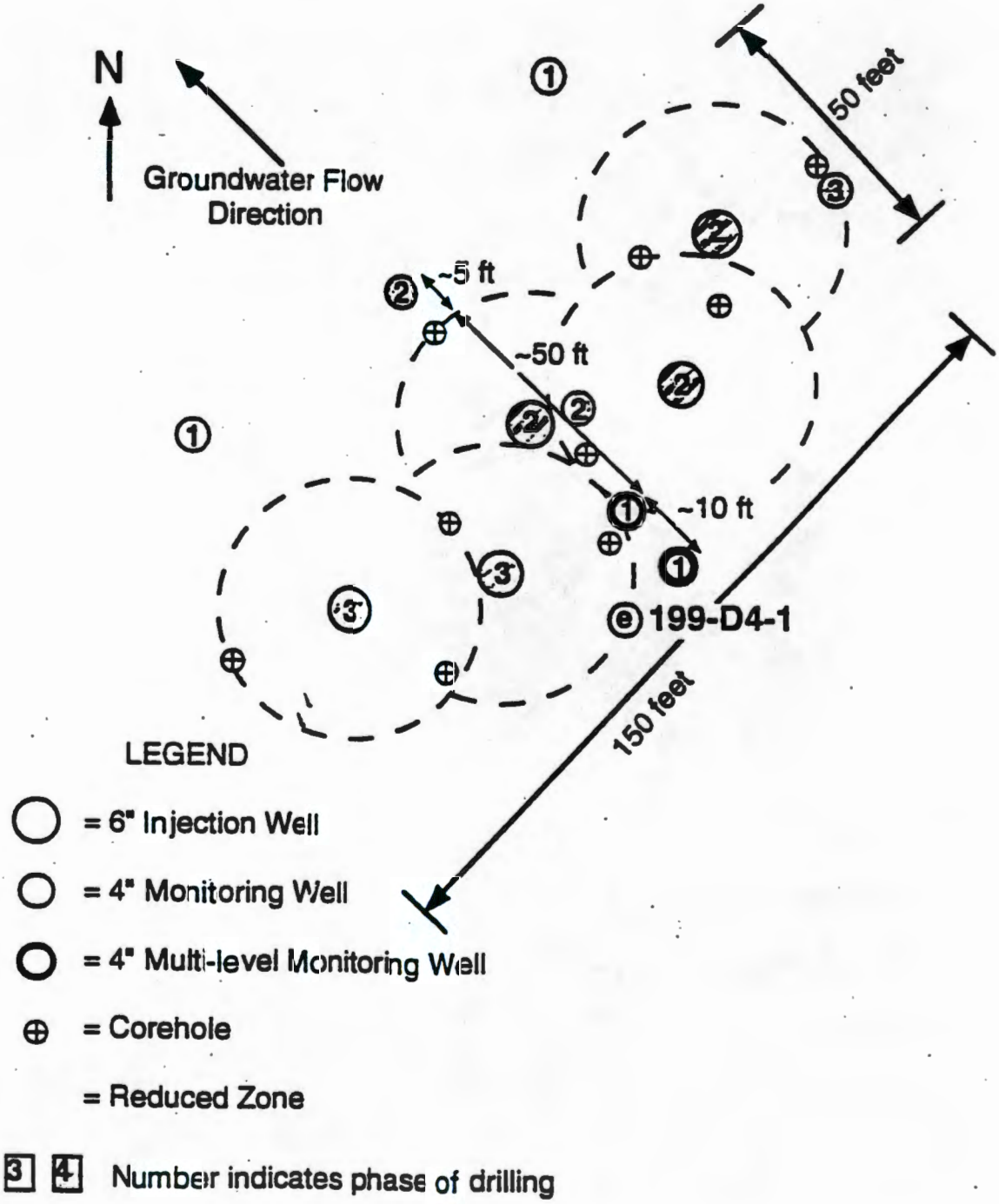
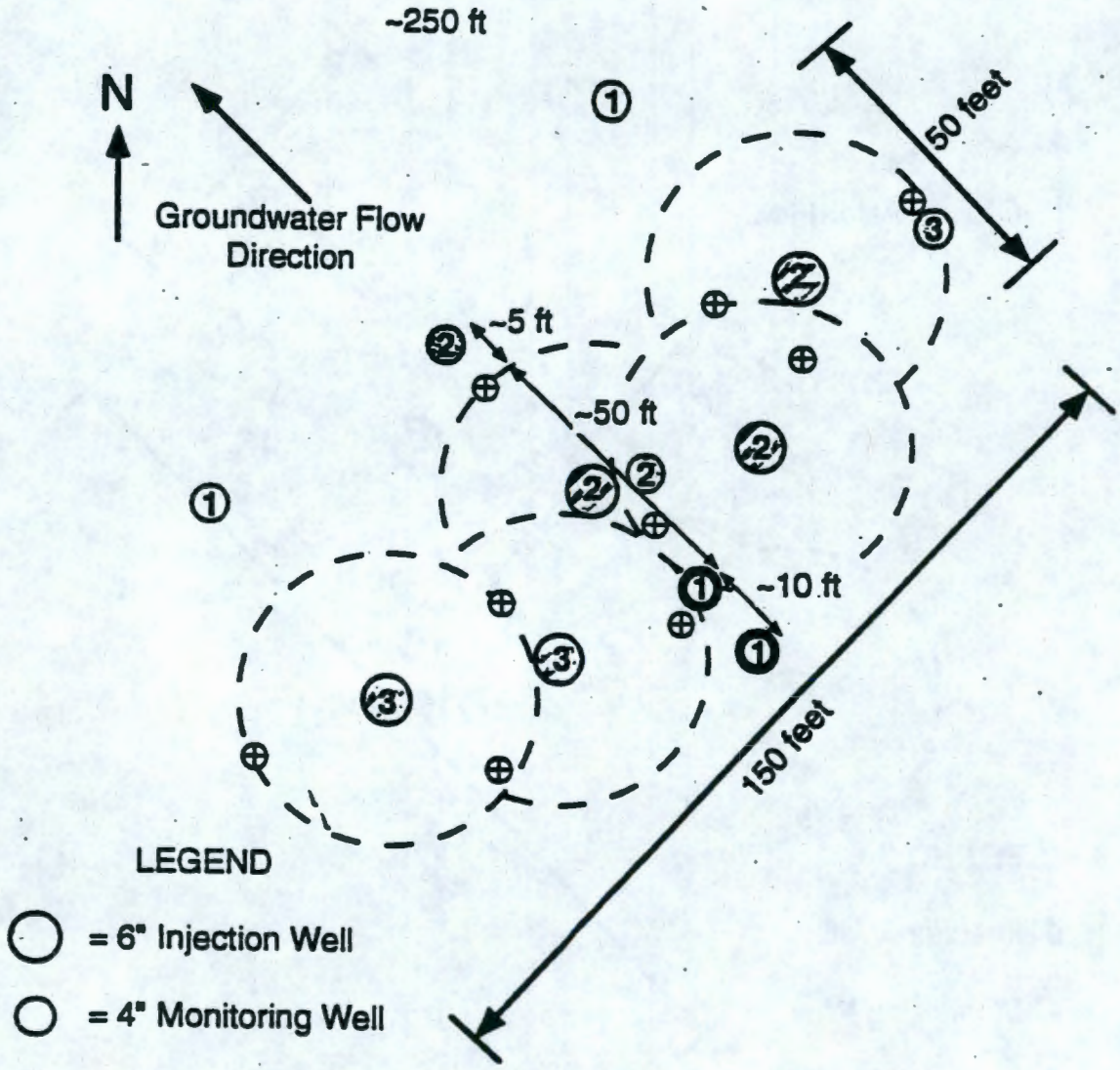

N
Groundwater Flow Direction
50 feet
~5 ft
~50 ft
199-D4-1
~10 ft
150 feet
LEGEND
= 6" Injection Well
= 4" Monitoring Well
= 4" Multi-level Monitoring Well
= Corehole
= Reduced Zone
1 2 3 4 Number indicates phase of drilling

Figure 4


N
Groundwater Flow Direction
50 feet
~5 ft
~50 ft
~10 ft
199-D4-1
150 feet
LEGEND
= 6" Injection Well
= 4" Monitoring Well
= 4" Multi-level Monitoring Well
= Corehole
= Reduced Zone
1 2 3 4 Number indicates phase of drilling

199-D4-1 ⓔ



LEGEND

= 6" Injection Well

= 4" Monitoring Well

= 4" Multi-level Monitoring Well

= Corehole

= Reduced Zone

1 2 3 4 Number indicates phase of drilling

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Environmental Restoration Contractor **ERC Team**

Interoffice Memorandum

Job No. 22192
Written Response Required? No
Closes CCN: N/A
OU: N/A
TSD: N/A
ERA: N/A
Subject Code: 8240

TO: R. C. Havenor X1-85

DATE: February 3, 1997

COPIES: See Below

FROM: D. D. Teel, Manager
Natural Resources & Risk Assessment
H0-02/372-9633

SUBJECT: **ECOLOGICAL REVIEW OF THE 100-D AREA REDOX MANIPULATION TEST (97-ER-002)**

This memo is in response to your request for an Ecological Review of the 100-D Area Redox Manipulation Test. The project consists of installing a series of 12 groundwater wells in an area of approximately 150' radius. The project is scheduled to begin in early February 1997. While the area is fairly level, some grading is required to create a more level surface and remove tumbleweeds.

The site was surveyed by Natural Resources on October 4, 1996; see Ecological Review 96-ER-036. The site is highly disturbed ground consisting of coarse gravels and sand, with only a small amount of weedy vegetation such as Russian thistle. Stegen (1994, Vegetation Communities Associated with the 100 Area Facilities on the Hanford Site, WHC-SD-EN-TI-216) also reports that this is part of a much larger area classified as "Disturbed, Non-Vegetated." No impacts to ecological resources will occur from construction of wells pads as identifiied on the attached map in this area.

If there are any major changes in the scope of activities that could result in any disturbance to soils or habitats outside the description of this project, please contact Ken Gano on 372-9316 and refer to the Ecological Review number given in the subject line.

SGW/DDT:dds

Attachment: Map

Copies: K. A. Gano H0-02
C. J. Kemp H0-02
A. J. Knepp H0-19
T. E. Marceau H0-02
J. J. Sharpe H0-03
S. G. Weiss H9-03
DDT: Letterbook H0-02
Document and Info Services H0-09

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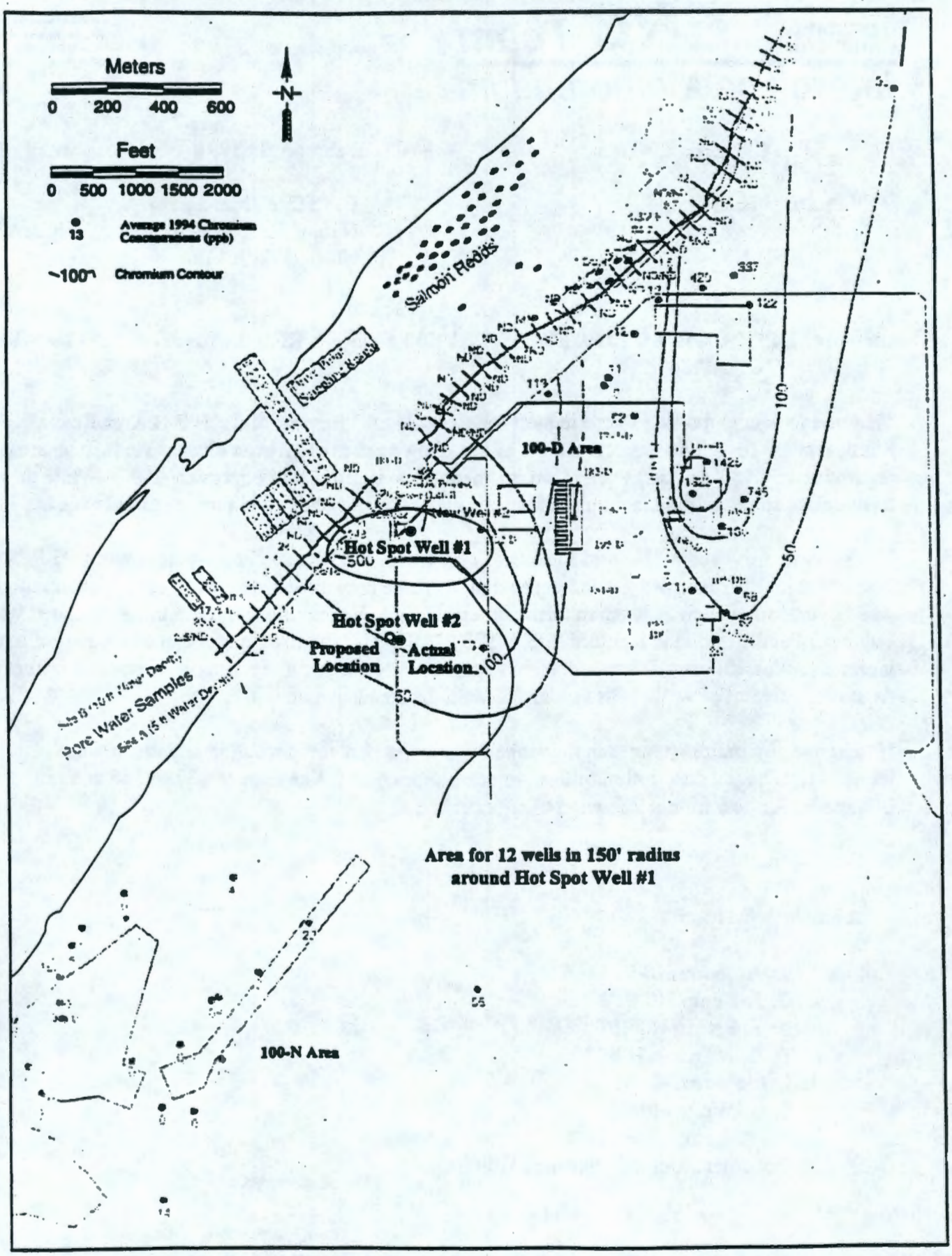
Figure 1. Location of Proposed Wells in 100-D Area



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ATTACHMENT B-5
BIOLOGIC REVIEW OF THE IN SITU REDOX MANIPULATION TREATABILITY TEST PROJECT, 100-D AREA (#97-100-011)

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Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

March 7, 1997

Mr. John S. Fruchter
Pacific Northwest National Laboratory
P. O. Box 999, MSIN K6-96
Richland, WA 99352

Dear Mr. Fruchter:

BIOLOGICAL REVIEW OF THE IN-SITU REDOX MANIPULATION TREATABILITY TEST PROJECT, 100D Area, #97-100-011

Project Description:

- Drill approximately 16 injection, monitoring, and sampling wells, and sub-surface injection of sodium dithionate to test in-situ redox manipulation technology.

Survey Objectives:

- To determine the occurrence in the project area of plant and animal species protected under the Endangered Species Act (ESA), candidates for such protection, and species listed as threatened, endangered, candidate, sensitive, or monitor by the state of Washington, and species protected under the Migratory Bird Treaty Act,

- To evaluate the potential impacts of disturbance on priority habitats and protected plant and animal species identified in the survey.

- To evaluate the potential impacts of the proposed subsurface injection on the aquatic ecology in the Columbia River near the proposed test site.

Survey Methods:

- Pedestrian and ocular reconnaissance of the proposed site was conducted by T.P. Hanrahan, M.R. Sackschewsky, and J.M. Becker on 25 April, 1996. The Braun-Blanquet cover-abundance scale (Bonham 1989) was used to determine percent cover of dominant vegetation,

- Priority habitats and species of concern are documented as such in the following: Washington Department of Fish and Wildlife (1993, 1994), Washington State Department of Natural Resources (1994), and for migratory birds, U.S. Fish and Wildlife Service (1985). Lists of animal and plant species considered Endangered, Threatened, Proposed, or Candidate by the USFWS are maintained at 50 CFR 17.11 and 50 CFR 17.12.

- An assessment of the potential impacts of the chemical injection on the aquatic ecology was performed by D.D. Dauble.

Survey Results:

- The proposed project location has been highly disturbed in the past, and the flora primarily consists of alien weedy species typical of disturbed areas,

- No migratory bird species were observed nesting in the vicinity of the proposed site,

- Movement of groundwater from the redox test site to the Columbia River is expected to be very slow (i.e., 25 to 50 ft/yr). At this rate, the treated plume would not likely intersect with the river shoreline until after several years. Thus, it is unlikely that there would be any short-term adverse impacts to aquatic biota in the shoreline adjacent to the test site. If the test is successful, potential chronic effects to river biota of Hanford-origin groundwater may be reduced from present conditions because chromium would be removed from the existing plume. Key concerns are lowered dissolved oxygen concentrations and elevated sulfate and manganese concentrations in the treated plume. However, any potential impacts to biota are expected to be minimal because of the low flux rate to the river, dilution from the hyporheic, and high rate of mixing with surface flows. Further, the zone of influence from the groundwater plume would be very small relative to river bottom available for aquatic production. Fall chinook salmon are not be expected to be impacted because spawning areas are not located in proximity to the test site. Planned monitoring of groundwater flow within shoreline areas adjacent to the test site will provide information relative to reoxygenation needs.

Considerations and Recommendations:

- No plant and animal species protected under the ESA, candidates for such protection, or species listed by the Washington state government were observed in the vicinity of the proposed site,
- No adverse impacts to other species or habitats of concern are expected to occur from the proposed action.

Sincerely,

CA Brandt, Ph.D.
Project Manager
Ecological Compliance Assessment

CAB:mrs

REFERENCES

Bonham, Charles D. 989. Measurements for Terrestrial Vegetation, John Wiley & Sons, Inc. pp.127-128.

U. S. Fish and Wildlife Service. 1985. Revised List of Migratory Birds; Final Rule. 50 FR 13708 (April 5, 1985).

Washington Department of Fish and Wildlife. 1993. Priority Habitats and Species. pp. 22.

Washington Department of Fish and Wildlife. 1994. Species of Special Concern in Washington. (April 1994).

Washington Department of Natural Resources. 1994. Endangered, Threatened & Sensitive Vascular Plants of Washington. (January 1994).

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APPENDIX C
SITE SPECIFIC SAFETY PLANS

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APPENDIX C
SITE SPECIFIC SAFETY PLANS

This Appendix includes:

1) the "Site Specific Health and Safety Plan for Drilling in Support of the In Situ Redox Manipulation" (BHI-01001) which was prepared by Bechtel Hanford, Inc. (BHI) for well installation activities; and

2) the "Site Specific Health & Safety Plan, In Situ Redox Manipulation Experiment, Well Injection" prepared by PNNL for Emplacement activities.

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