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In Situ REDOX Manipulation: Site Evaluation for Chromate Remediation in Groundwater

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CONTENTS

1.0 INTRODUCTION 1
1.1 IN SITU REDUCTION AND OXIDATION MANIPULATION TECHNOLOGY DESCRIPTION 1
1.2 IN SITU REDUCTION AND OXIDATION MANIPULATION PROJECT DESCRIPTION 1
1.3 CURRENT REMEDIATION OF GROUNDWATER 2

2.0 EVALUATION 2
2.1 BACKGROUND 2
2.2 PURPOSE AND OBJECTIVES 2
2.2.1 Cr^{6+} Contamination in Aquifer 3
2.2.2 Fe^{3+} Concentration in Aquifer Sediments 7
2.2.3 Proximity to River 7
2.2.4 Hydrogeology 10
2.2.5 Above/Underground Structures 12

3.0 CONCLUSION 13

4.0 REFERENCES 15

APPENDICES:

A GROUND PENETRATING RADAR A-1

FIGURES:

1. 100-HR-3 Operable Unit Monitoring Well Locations 4
2. 100-HR-3 Chromium (VI) Well Location Map 5
3. 100-D Area Chromium (VI) Groundwater Contaminant Plume, 1994 to 1995 Data 6
4. 100-H Area Chromium (Filtered) Distribution in Groundwater 8
5. Wells in Plume Vicinity 9
6. 105-D and 105-DR Reactor Area Geologic Profile 11
7. Detailed Ground Penetrating Radar Survey of the 108-D Area 14
8. 100-D/DR Area 16

TABLES:

1. Aquifer Specifics of Wells at the 100-D Area 10

ACRONYMS

COPC	contaminant of potential concern
EM	electromagnetic
FY	fiscal year
GPR	ground penetrating radar
IRM	interim remedial measure
ISRM	In Situ REDOX Manipulation
LWDF	Liquid Waste Disposal Facility
MTCA	Model Toxic Control Act
PNL	Pacific Northwest Laboratory
RCRA	*Resource Conversation and Recovery Act of 1976*
REDOX	Reduction and Oxidation
WHC	Westinghouse Hanford Company

1.0 INTRODUCTION

In Situ Reduction and Oxidation (REDOX) Manipulation (ISRM) technology involves creating a permeable subsurface treatment zone to reduce chromate in groundwater. The ISRM technology can be further applied to destroy subsurface contaminants in groundwater (e.g., nitrates, organics [specifically carbon tetrachloride]) and to temporarily immobilize other contaminants (e.g., technetium and uranium). Other methods (e.g., pump and treat) have been developed to treat contaminants ex situ but may not be as effective in treating areas of dispersed groundwater contamination. ISRM is being implemented as a treatability test to determine the feasibility of chromate remediation in situ. This document assesses if the 105-D Reactor Area location is potentially suitable for implementing REDOX as a method for remediating chromate-contaminated groundwater. Data for the 100-H Area are also included in this report as another potential location.

1.1 IN SITU REDUCTION AND OXIDATION MANIPULATION TECHNOLOGY DESCRIPTION

The goal of the ISRM technology 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 to ferrous iron 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 (Fe^{3+}) to ferrous iron (Fe^{2+}) within the aquifer sediments. Chromate ($Cr_2O_7^{2-}$), which is anionic in nature and soluble in groundwater, contains the 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 in the groundwater [$Cr(OH)_3$]. A more detailed description of the ISRM project and the associated ISRM technology can be found in the *Test Plan for the 100-H Area In Situ REDOX Manipulation Experiment* (Fruchter et al. 1995).

1.2 IN SITU REDUCTION AND OXIDATION MANIPULATION PROJECT 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, which included bench-scale and field-scale experiments, was used during development of the ISRM technology. The intent of ISRM involves constructing a permeable subsurface treatment zone to determine feasibility and compare costs with existing remediation technologies. If this technology proves successful, it may result in cost savings when compared to pump-and-treat groundwater plume remediation methods. The startup costs of ISRM are comparable to a pump-and-treat system, but once the permeable treatment barrier is emplaced, there could be little maintenance or long-term costs except for periodic groundwater monitoring for performance assessment. In addition, the use of ISRM in this treatability test will provide information to allow the technology to be further developed for possible application at the Hanford Site and other locations.

1.3 CURRENT REMEDIATION OF GROUNDWATER

The focus of groundwater remediation at the Hanford Site is the use of interim remedial measures (IRMs) to address specific groundwater contaminants and plumes. As part of the IRMs, or as part of the final remedy selection process that will follow, innovative treatment technologies may be implemented in place of, or in combination with, pump-and-treat technologies.

Pump and treat has been proven to remove mass and contain plumes; however, it requires continual operational costs (e.g., pumping and treatment) as well as standard maintenance and monitoring. These continual operational aspects result in increased costs for this technology. The benefits of the ISRM treatment technology include the following:

- Implementation of innovative treatment technologies
- Direct in situ treatment of the contaminant
- Information for the further development of in situ treatment technology for inorganics, organics, and nitrates
- Potential reduction in remediation costs because of increased efficiency (i.e., no routine operational costs except for monitoring)
- Limitation of field activities to the short time required for reduction to occur.

2.0 EVALUATION

2.1 BACKGROUND

Sodium dichromate was utilized at the Hanford Site as an anticorrosion agent in reactor cooling systems (2 mg/L sodium dichromate [Na_2Cr0_7]) (Richards 1953) and for decontamination activities (Thornton 1995). Reactor coolant water handling facilities and liquid waste disposal trenches were contaminated with water that contained low concentrations of radionuclides and potentially hazardous species including chromium (DOE-RL 1994). Chromium detected in groundwater samples is determined to be a contaminant of potential concern (COPC) in groundwater as a result of this past practice and is listed as a target contaminant for groundwater remediation (DOE-RL 1995).

2.2 PURPOSE AND OBJECTIVES

This report provides available data to assist in the location for the implementation of the REDOX treatability test. Chromium has been determined to be a COPC at the 100-HR-3 Groundwater Operable Unit. The most suitable location to implement this treatability test would be where the presence of chromate exists in high concentration, so that the feasibility of chromate remediation in groundwater can be determined. An IRM has been proposed to address this contaminant through a proposed plan for the 100-HR-3 Operable Unit. Because the ISRM has the potential to reduce costs and help accelerate

remediation, it is proposed that a site in the 100-HR-3 Operable Unit be used for this treatability test. The following available data are key to locating the REDOX site:

- Presence of Cr^{6+} contamination in aquifer
- Sufficient layer silicate fraction contains structural Fe^{3+} in aquifer sediments (>0.05% of total sediment fraction)
- Distance of Cr^{6+} contamination from the river
- Aquifer modeling (transmissivity, lateral extension of confining unit, hydraulic gradient)
- Absence of aboveground/underground structures.

2.2.1 Cr^{6+} Contamination in Aquifer

Considerations for the ISRM treatability test include the presence of chromate in the unconfined aquifer. Chromium has been determined to be a COPC at 100-HR-3 and is the focus for groundwater remediation. At the 100-D Area, the chromium plume is fairly widespread and is difficult to define because of the limited distribution and number of monitoring wells and their associated analyses (DOE-RL 1994). Figure 1 shows monitoring wells installed at the 100-D and 100-H Areas that comprise the 100-HR-3 Groundwater Operable Unit. Figure 2 shows the distribution of chromium (VI) and the associated wells within the 100-HR-3 Groundwater Operable Unit. Figure 3 shows 1994 to 1995 chromium (VI) groundwater contaminant plume data from groundwater wells within the 100-D Area that are monitored as part of the 100-HR-3 groundwater monitoring network.

The highest concentration of filtered chromium (VI) detected at the 100-D Area was 1,392 ppb from well 199-D-14 (see Figure 3), located directly downgradient from the 105-D Reactor. The past existence of a sodium dichromate pump station located southeast of well 199-D5-14 and the presence of reactor effluent lines running into the Liquid Waste Disposal Facility (LWDF) may have contributed as potential sources. No wells are located downgradient of 199-D5-14 to determine the approximate northern extent of the chromium plume. This will remain undetermined unless further characterization of this area can be accomplished.

Samples from well 199-D2-6 indicate the presence of chromium (VI) in groundwater downgradient of the 118-D-2 Solid Waste Burial Ground. The most recent analysis indicates well 199-D2-6 has a (filtered) chromium concentration of 146 ppb. Because no other monitoring wells are located within the proximity of well 199-D2-6, there is little control on the extent and distribution of the chromium plume surrounding well 199-D2-6. Current discussion regarding the concentration of chromium (VI) for well 199-D2-6 suggests the possibility of a chromium (VI) plume north of well 199-D2-6. Because this well is located upgradient of the other groundwater monitoring wells included in the 100-HR-3 groundwater monitoring network, the source of the chromium (VI) plume is undetermined until there is further characterization of this area.

Total chromium (filtered) samples from wells 199-D8-53 and 199-D8-54A, located downgradient of the 100-D Area liquid waste disposal facilities, indicate 350 ppb and 442 ppb, respectively (see Figure 2). Groundwater samples may indicate the presence of chromium (VI) within the aquifer; however, this location is not suitable for REDOX because of the proximity of the wells to the river.

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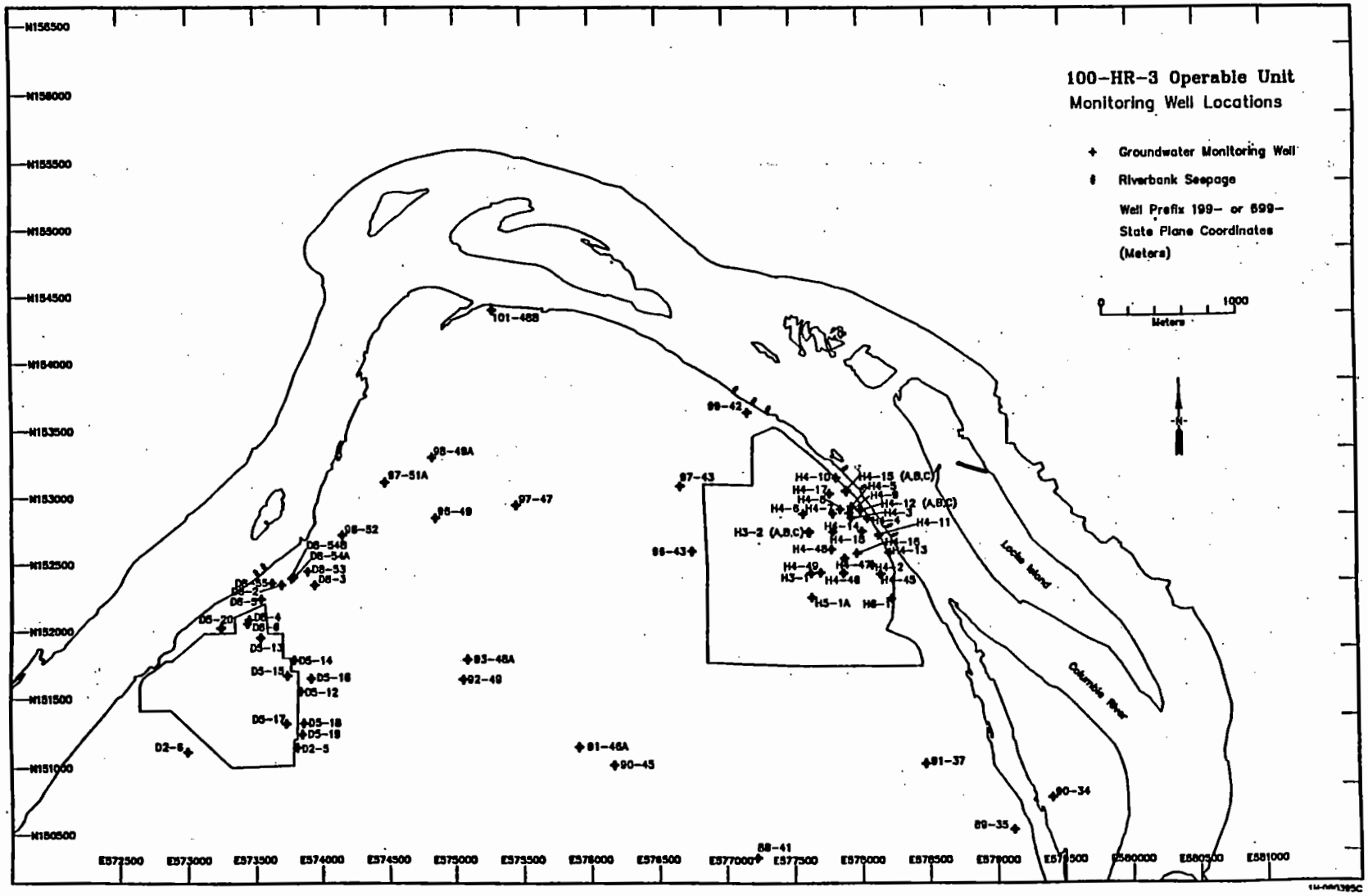
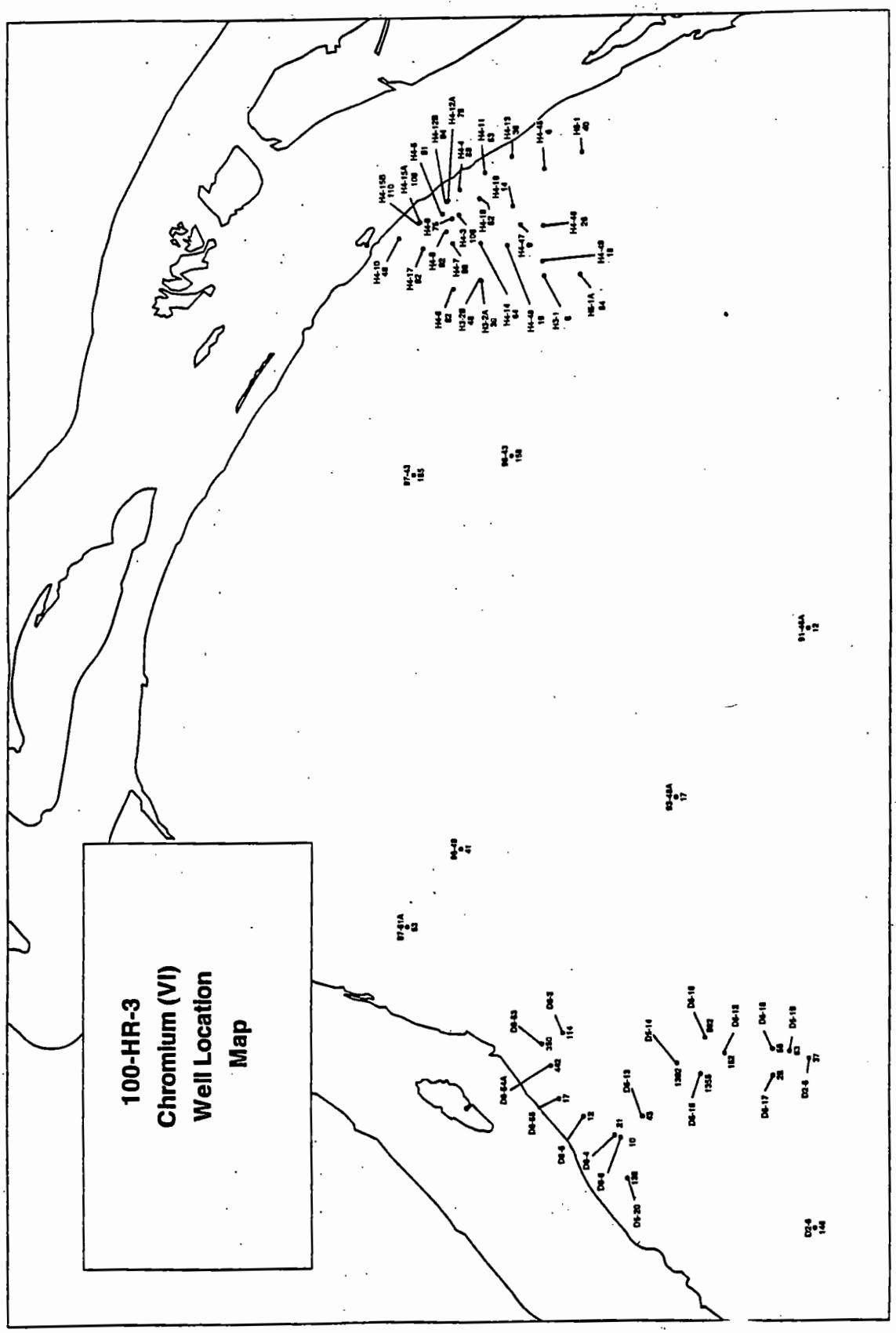


Figure 1. 100-HR-3 Operable Unit Monitoring Well Locations.

Figure 2. 100-HR-3 Chromium (VI) Well Location Map.



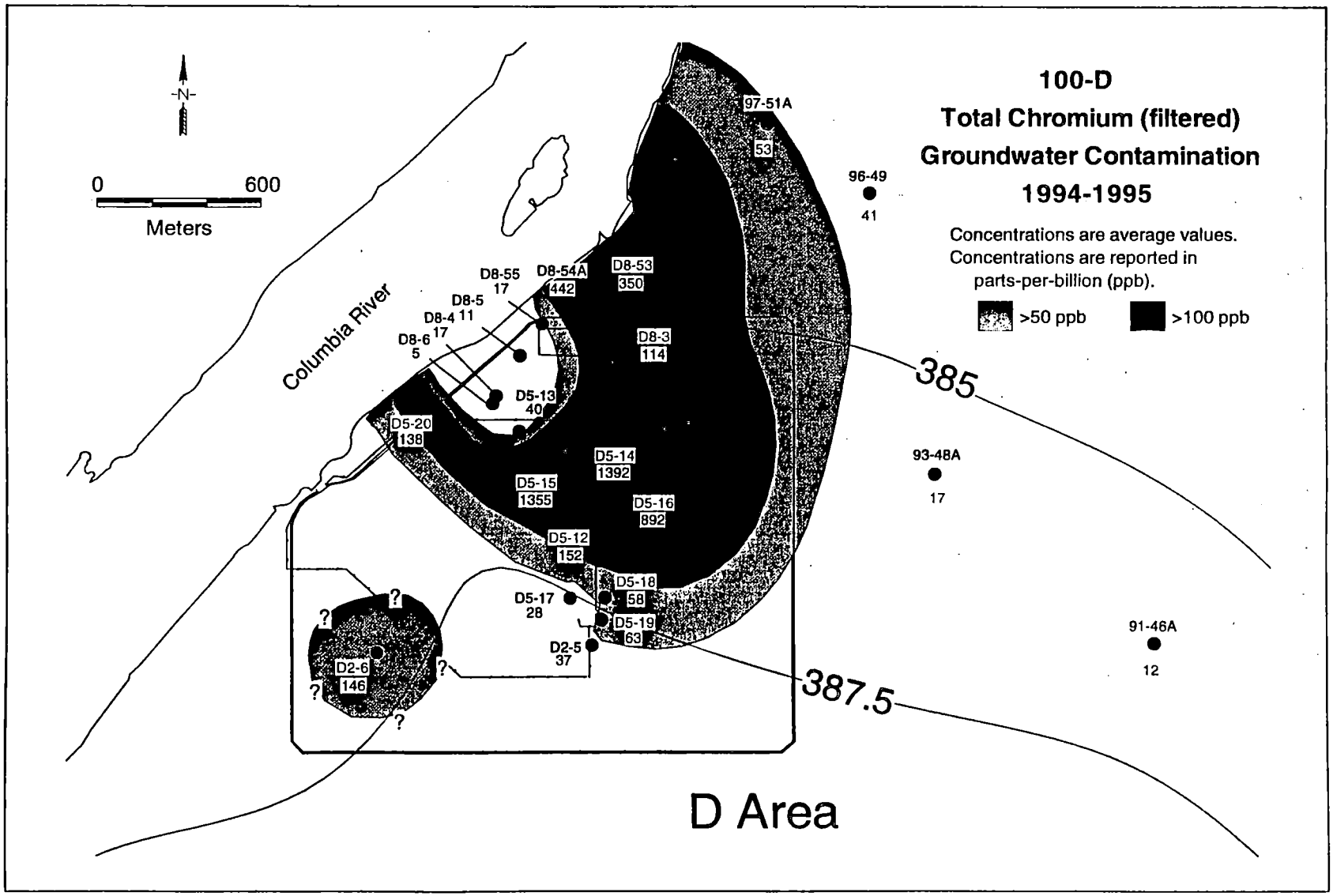


Figure 3. 100-D Area Chromium (VI) Groundwater Contaminant Plume, 1994 to 1995 Data.

Figure 4 shows total chromium (filtered) in the unconfined aquifer at the 100-H Area. Wells sampled are part of the 100-HR-3 groundwater monitoring network and the 183-H *Resource Conservation and Recovery Act* (RCRA) groundwater monitoring network. Well 199-H4-15A, located near the Columbia river at the 100-H Area, has the highest concentration of chromium, 110 ppb. However, this location is not suitable for REDOX because of the proximity of the wells to the river.

Groundwater data on the 100-HR-3 Groundwater Operable Unit indicate that concentrations of chromium (ppb) are present in the unconfined aquifer at 100-D Area, 100-H Area, and the 600 Area. Assessment of chromium data from wells 199-D5-12, 199-D5-14, 199-D5-15, and 199-D5-16 in the 100-D Reactor area indicate that well 199-D5-14 has an elevated level of chromium over time (Figure 5). Based on these data, the only suitable location for chromium remediation would be within the vicinity of well 199-D5-14. There are no data available on the vertical distribution of chromium within the unconfined aquifer underlying the 100-HR-3 Area.

2.2.2 Fe^{3+} Concentration in Aquifer Sediments

To create a subsurface permeable treatment zone, the sodium dithionite injection must reduce the ferric iron within the clay minerals of the aquifer material. Naturally occurring Fe^{3+} content in the clay in the more transmissive portions of these sediments should be 0.05% of the total sediment fraction and should be associated with layer silicate clays.

Samples taken from 73.5 to 95 ft from well 199-D5-19 at the 100-D Area indicate that the average percentage of Fe^{3+} in the Ringold Formation could be as high as 0.88% based on the maximum assumption of 19 wt% clay. Wells 699-91-46 and 699-93-48, located in the 600 Area between the 100-D and 100-H Areas, have a percent layer silicate iron content of 1.8% and 1.9%, respectively. Well 199-H5-1 at the 100-H Area Pacific Northwest Laboratory (PNL) ISRM project site has a silicate iron content of 1.3%.

Analyses of clays that are within the Ringold Formation and the Hanford formation and collected around the Hanford Site by PNL indicate ferric iron quantities averaging greater than 1% iron by weight.

Sediment samples were taken from the Ringold Formation at the 100-H Area ISRM field test site. These samples were analyzed for iron (III) using the colorimetric method. Analytical results indicate an iron (III) content of 0.73% by weight for Ringold Formation sediments (Vermeul et al. 1995).

Data indicate that the average percent of Fe^{3+} in the 100-D and 100-H Areas is above the minimum percent needed to support reducing conditions. However, site-specific Fe^{3+} data may be needed to determine if the potential treatability test site has the percent Fe^{3+} needed to support reducing conditions.

2.2.3 Proximity to River

The goal of ISRM is to create a permeable treatment zone downgradient of a contaminant plume. However, a permeable treatment zone of reducing conditions near the river may produce temporary anoxic conditions within the groundwater that may eventually reach the river. Areas along the shoreline should not be considered based on the aquifer/river communication and conditions produced by ISRM.

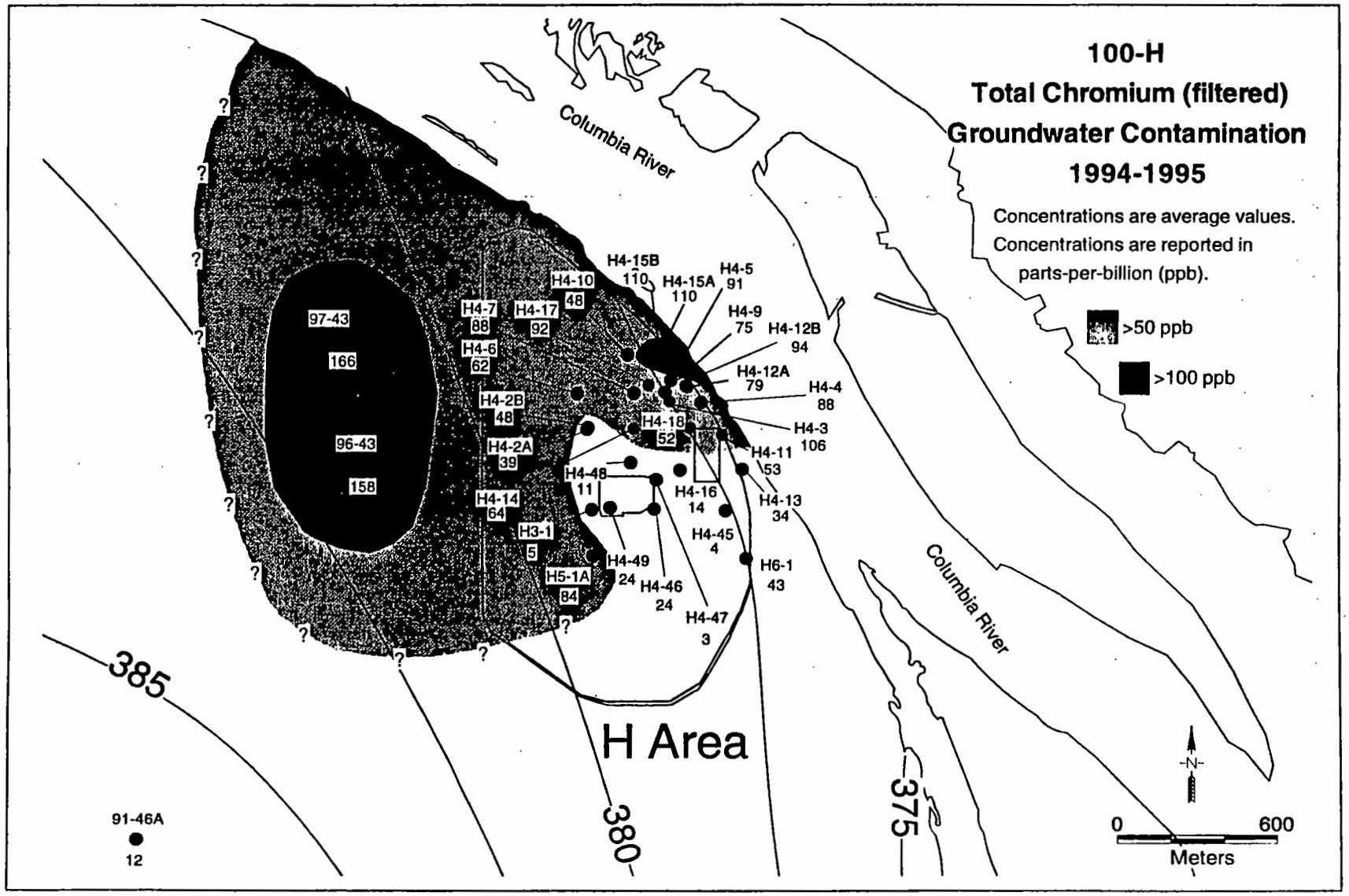
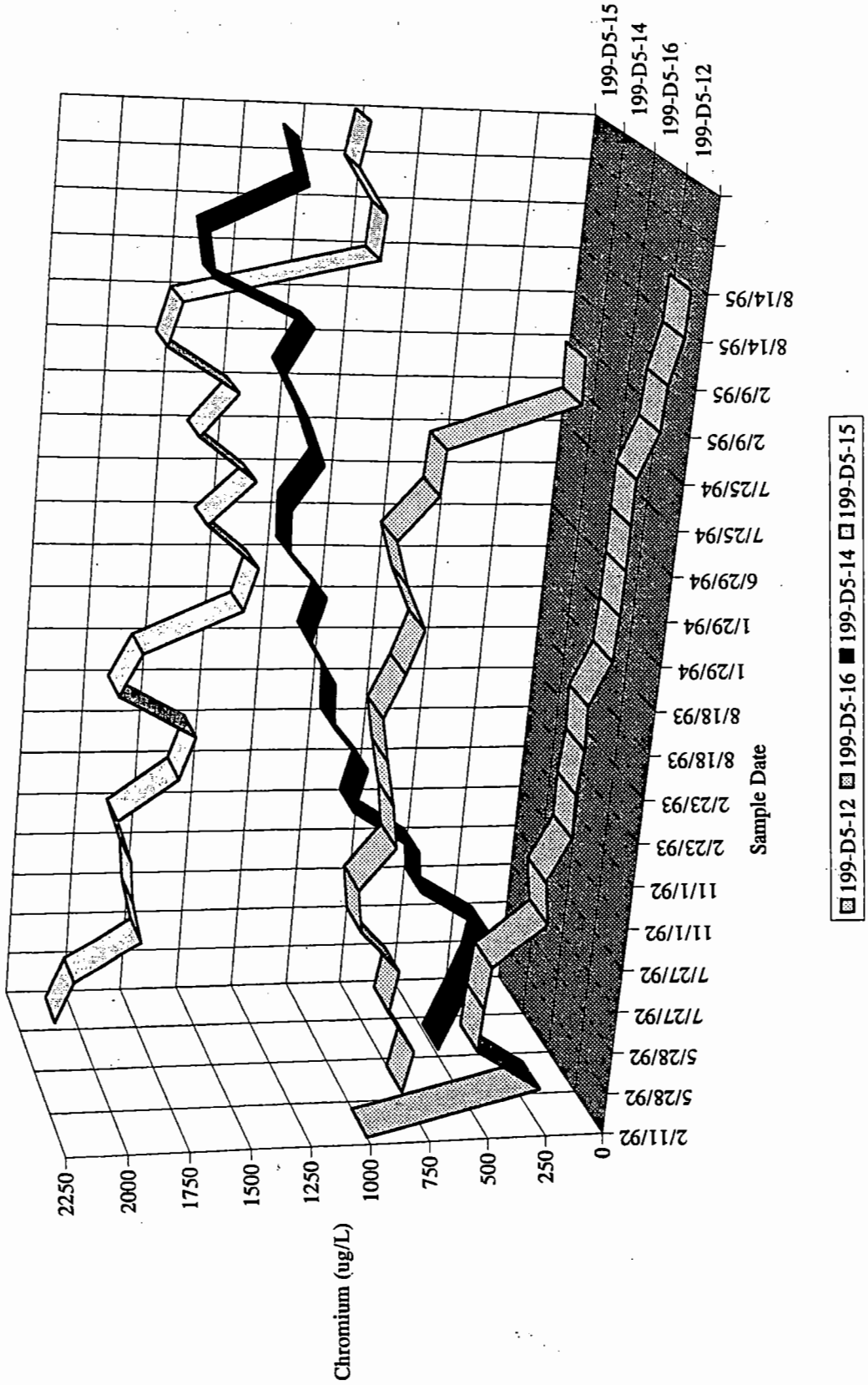


Figure 4. 100-H Area Chromium (Filtered) Distribution in Groundwater.

Figure 5. Wells in Plume Vicinity.



Groundwater within the 100-D Area generally flows toward the river, but flows parallel during high river stage(s). High river stage commonly influences wells inland, especially at the 100-D Area where the wells are influenced up to 1,950 ft inland (DOE-RL 1994). This phenomenon is the result of river interaction with the unconfined aquifer.

The proximity to the river is a limiting factor for implementing the treatability test at the 100-H Area. Wells at the 100-H Area that are indicated to have chromium (VI) of significance include well 199-H4-15A, located near the 100-H Area shoreline. Therefore, this location will be precluded as a potential location for the fiscal year (FY) 1996 treatability test.

Wells located in the 105-D and 105-DR Reactor plume are on the average of 3,000 ft from the river. Locating an ISRM treatability test site in either one of these areas would not be influenced by groundwater-river interaction.

2.2.4 Hydrogeology

Hydrogeology of the treatability test area is essential in determining the design of the REDOX barrier. Several specifics that are considered include the extent of the aquifer bottom or confining unit, formation transmissivity, aquifer stratigraphy, saturated thickness of the aquifer, and hydraulic gradient.

The unconfined aquifer at the 100-D Area exists mainly in the Ringold Formation (DOE-RL 1994). The Ringold Formation consists of several facies: fluvial gravel, fluvial sand, overbank deposits-paleosols, lacustrine deposits, and basaltic alluvium. The upper 50 ft of the Ringold Formation consists of fluvial gravel and overbank, or paleosol sediments. Fluvial gravels comprise the top of the Ringold Formation, except in the area north of the 100-D Area retention basins. Overbank muds and paleosols underlie the gravels. Only well 199-D-54B in the 100-D Area penetrates below these muds (Lindsey and Jaeger 1993). The Ringold Formation Unit E and the upper mud directly underlie the Hanford formation at the 100-D Area. Figure 6 shows the geologic profile of the 105-D and 105-DR Reactor area (D-D'). Depth to water, aquifer bottom, and aquifer thickness were determined from wells within the 100-D Area chromium (VI) plume (Table 1). Wells 199-D5-14 and 199-D5-16 were not drilled into the confining unit; therefore, the aquifer thickness could not be determined. Current groundwater depths of wells 199-D5-14, 199-D5-15, and 199-D5-16 cannot be determined because of pump-and-treat operations. Pump-and-treat operations would have to cease to allow the aquifer to recover before obtaining static water levels.

Table 1. Aquifer Specifics of Wells at the 100-D Area.

Well	Water (fbgs)	Aquifer Bottom (fbgs)	Aquifer Thickness (ft)	Hydraulic Conductivity (ft/day)
199-D2-6	84.9 5/95	103	18.1	40
199-D5-14	N/A	N/A	N/A	30
199-D5-15	N/A	101	18.1	N/A
199-D5-16	N/A	N/A	N/A	10

NOTE: The approximate hydraulic gradient in the vicinity of the 105-D Reactor is 4.0×10^{-4} (gradient can vary to 10^{-3} depending on river stage influence).

fbgs = feet below groundsurface
N/A = not available.

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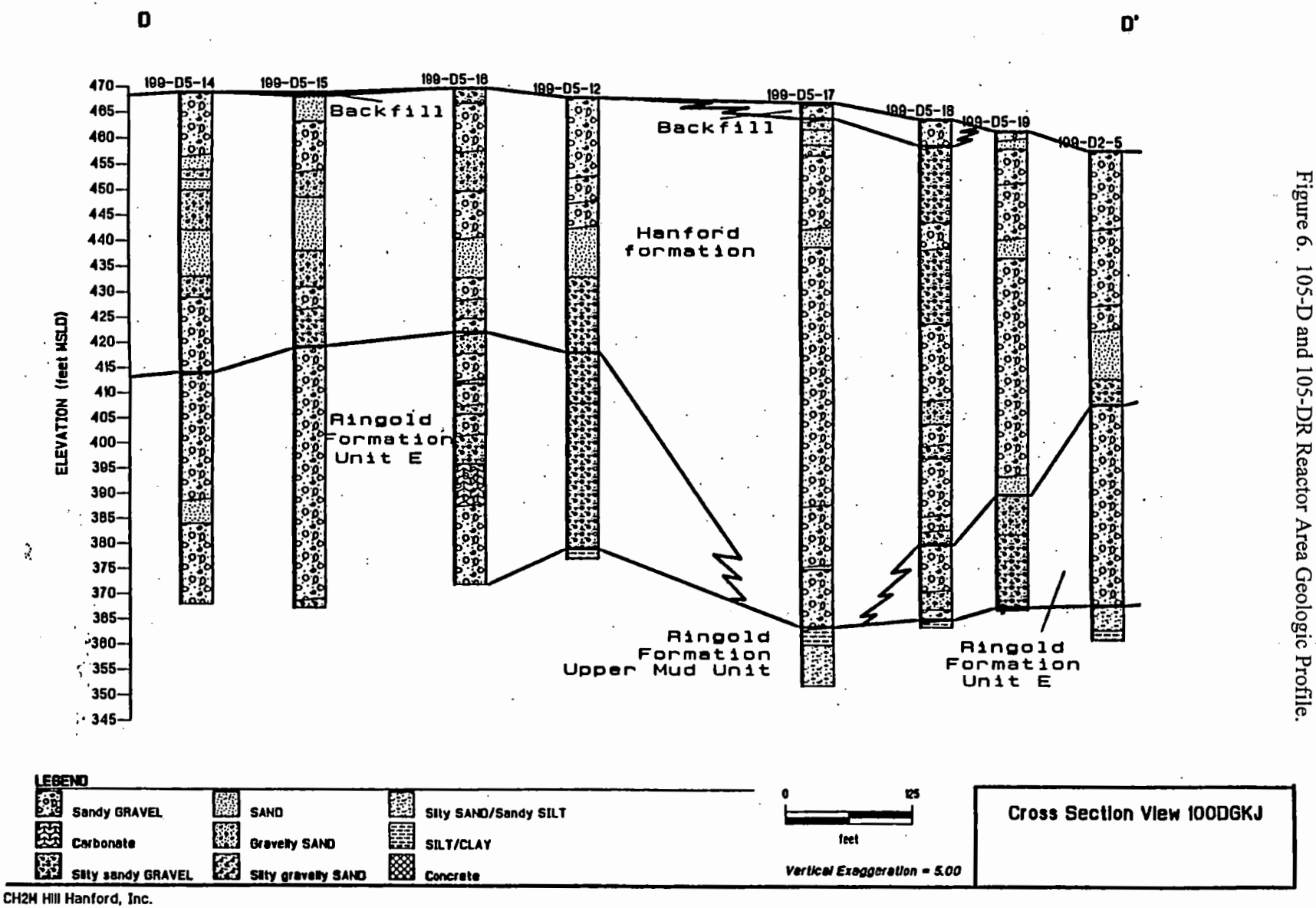

Figure 6. 105-D and 105-DR Reactor Area Geologic Profile.

Groundwater flow direction in the vicinity of the 105-D and 105-DR Reactors is not clearly defined because of the interpreted presence of a "groundwater divide." The chromium plume within the 100-D Area behaves like a single entity, although limited distribution of monitoring wells in this area makes analysis somewhat subjective. The source of this plume appears to be located near the 105-D Reactor (DOE-RL 1994).

Limited amounts of hydrogeologic information have been obtained concerning the unconfined aquifer within the 100-D Area. The limited amount of available data does not provide comprehensive information on aquifer properties relative to implementing ISRM. Most of the data that are available are of questionable validity. Because no complete, comprehensive aquifer property data are available for the 100-D Area, aquifer properties would have to be determined in conjunction with the initial phases of the treatability test.

2.2.5 Above/Underground Structures

The figure in Appendix A represents the compilation of the interpretations from four ground penetrating radar (GPR) surveys. The surveys were conducted in 1991 and 1992 in support of the Westinghouse Hanford Company (WHC) drilling program. The objective of each individual survey was to help determine appropriate locations for monitoring/characterization wells in support of 108-D, D-5-14, 116-D-3, and 116-D-4. Survey results were used to help avoid unexpected subsurface features during drilling. No formal reports were required or generated, but the original interpretation maps and data have been maintained in the geophysical files. These data and individual maps were used in this compilation to assess any subsurface obstruction that would possibly be encountered during emplacement of the REDOX barrier within the 105-D Reactor chromium (VI) plume.

2.2.5.1 Ground Penetrating Radar Methodology. GPR is a noninvasive, environmentally safe method of detecting, locating, and/or mapping shallow subsurface features. The method utilizes a transducer to transmit FM-frequency electromagnetic (EM) energy into the ground. Interfaces in the ground, defined by contrasts in dielectric constants, magnetic susceptibility, and to some extent, electrical conductivity, reflect the transmitted energy. The GPR system measures the travel time between transmitted pulses and arrival of reflected energy. Buried objects such as pipes, barrels, foundations, and wires can cause the transmitted energy to be reflected towards a receiving antenna. Geologic features such as crossbedding, caliche horizons, paleosols, and clays can also cause reflections of a portion of the EM energy. The velocity of the EM energy is controlled primarily by the dielectric constant and magnetic susceptibility of the medium. Values of EM velocity for depth calculations are determined by experience in an area, by ties to known buried reflectors, and from knowledge of the subsurface medium.

The maximum depth of investigation varies at each site and is a function of the transmitter power, receiver sensitivity, frequency of the antenna, and attenuation of the transmitted energy. The attenuation of the energy is primarily a function of the local soil conditions. High attenuation and, therefore, small penetration depths of the EM energy typically occur where ground conductivity is greater than 10 mS/m and/or in areas with numerous reflective interfaces. Depth of investigation is also affected by highly conductive material such as metal drums and pipes, which essentially reflect all the energy. The method cannot see directly below areas of highly reflective material because all the energy is reflected.

The reflected energy provides the means for mapping the subsurface features of interest, whether man-made or geologic. Display and interpretation of GPR data are similar to that of seismic reflection data

(e.g., data are displayed as horizontal distance versus time and depict pseudo cross sections of the earth). The end product is a plan view map that shows the location and depth of features detected within the survey area. The interpretation is influenced by the objectives of the survey, the experience of the interpreter, and the data processing techniques used. In some areas, interpretations can be straightforward, but a highly variable subsurface often yields complex data that are difficult to interpret.

The GPR equipment used at these sites was a Geophysical Survey Systems, Inc. Subsurface Interface Radar System 8 (a registered trademark of Geophysical Survey Systems, Inc.). A 300-MHz antenna with a recording window of 100 ns two-way travel time was used at the 108-D Building site. A 100-MHz antenna with recording windows ranging from 100 to 150 ns was used in the other GPR surveys included in this compilation. Maximum calculated depths of usable data varied from 10 to 14 ft for these surveys.

The detailed survey over the 108-D Building site was collected on a 5-ft by 5-ft grid. The other surveys compiled here were collected on a 10-ft by 10-ft grid with the lower resolution 100-MHz antenna.

Distances were measured and posted in feet for this work. The survey grids were "tied" to the perimeter fence. The southwestern corner of the combined grid is designated N100/E100 and serves as the "origin" for the survey locations. The letters "E" and "N" refer to a direction that trends generally east or north, respectively. The number refers to a distance in feet. For example, grid point E130/N120 lies 30 ft east and 20 ft north of grid point E100/N100.

2.2.5.2 Discussion. Several prominent features are evident in Figure 7 and in the figure in Appendix A. Four buried linears were detected. Two are north-south linears, 8 and 10 ft below the surface, that trend along E180 and E240, respectively. Excavation boundaries can be determined for portions of these two linears, which probably represent effluent lines. A third linear, buried about 3 ft, trends east-west along N64. It terminates around E225, presumably feeding a trench or pit. The fourth linear trends east-west along N270, buried 4 ft below the surface.

Throughout the portion of the survey area that is east of the perimeter fence are scattered isolated anomalies at various, but generally shallow, depths. These types of anomalies typically represent scattered "construction" debris.

The survey area west of the perimeter fence is dominated by concentrated debris and strong shallow reflectors. The 108-D Building was located here, and the anomalies probably represent portions of concrete slabs and building debris that were not removed during its demolition.

3.0 CONCLUSION

According to the available information, the 100-D and 100-H Areas are both viable locations for ISRM technology. The intent of this report was to evaluate potential sites through the use of reliable data that are key to implementing ISRM to determine a suitable test site.

Chromium contamination in the 100-HR-3 Groundwater Operable Unit has been demonstrated to be the highest priority groundwater contaminant in the operable unit because of its potential human health and ecological impacts (DOE-RL 1994). The former sodium dichromate pump station upgradient from well

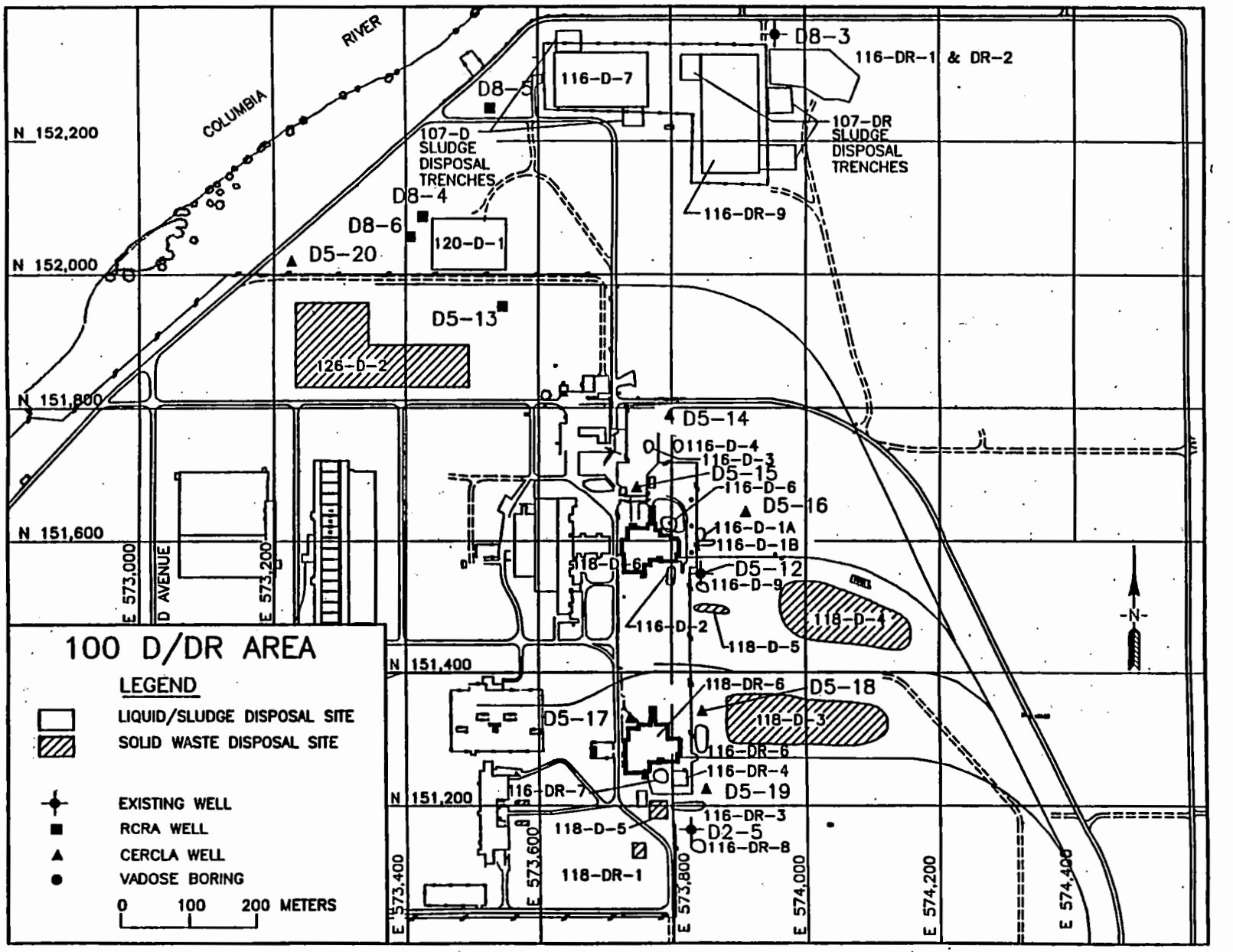

Figure 7. Detailed Ground Penetrating Radar Survey of the 108-D Area.

199-D5-14 and effluent lines from reactor operations explain the presence of chromium within the vadose zone and unconfined aquifer at the 100-D Area. Based on the available data for the 100-HR-3 Area, a location in the proximity of well 199-D5-14 would be most suitable for the emplacement of the ISRM site. Well 199-D5-14 has the highest concentration of chromate at the 100-D Area (1,392 ppb). The distance to the Columbia River from this location is approximately 3,000 ft. The aquifer exists mainly in the Ringold Formation; therefore, it provides the necessary Fe^{3+} concentrations to support reducing conditions. Additional data may be needed to quantify site-specific Fe^{3+} concentrations. These data could be obtained during an initial field phase. GPR of this area indicates subsurface disturbance, but no hazardous subsurface structures would impede the emplacement of injection and monitoring wells to create the REDOX barrier.

The 100-D Area pump-and-treat system began operations during FY 1995 to treat chromium (VI)-contaminated groundwater within the 105-D Reactor plume. Groundwater wells 199-D5-14, 199-D5-15, and 199-D5-16 are used for extraction of chromate-contaminated groundwater. These wells are located at the approximate forefront of the high-concentration 105-D Reactor chromate plume. The spacing, location, and pumping rates at these existing pump-and-treat wells, relative to estimates of ambient groundwater flow (i.e., without pumping), are conducive to site location. It appears that a 200-ft-long, 50-ft-wide reduced zone (emplaced through the use of closely spaced sodium dithionite injection/withdrawal wells) could be created in a downgradient chromate plume pathway with the pump-and-treat wells pumping or shut down. The average pumping rate of the system during the extraction process is low enough not to create a zone of influence that would interfere with the reduction barrier.

As a result of this site evaluation, it has been determined that there are areas of insufficient data relative to the emplacement of the REDOX barrier within the area of 199-D5-14 (Figure 8). The data gaps that are recognized include geohydrologic data, vertical distribution of chromate, and plume definition. This information would have to be acquired during the initial phase of the treatability test.

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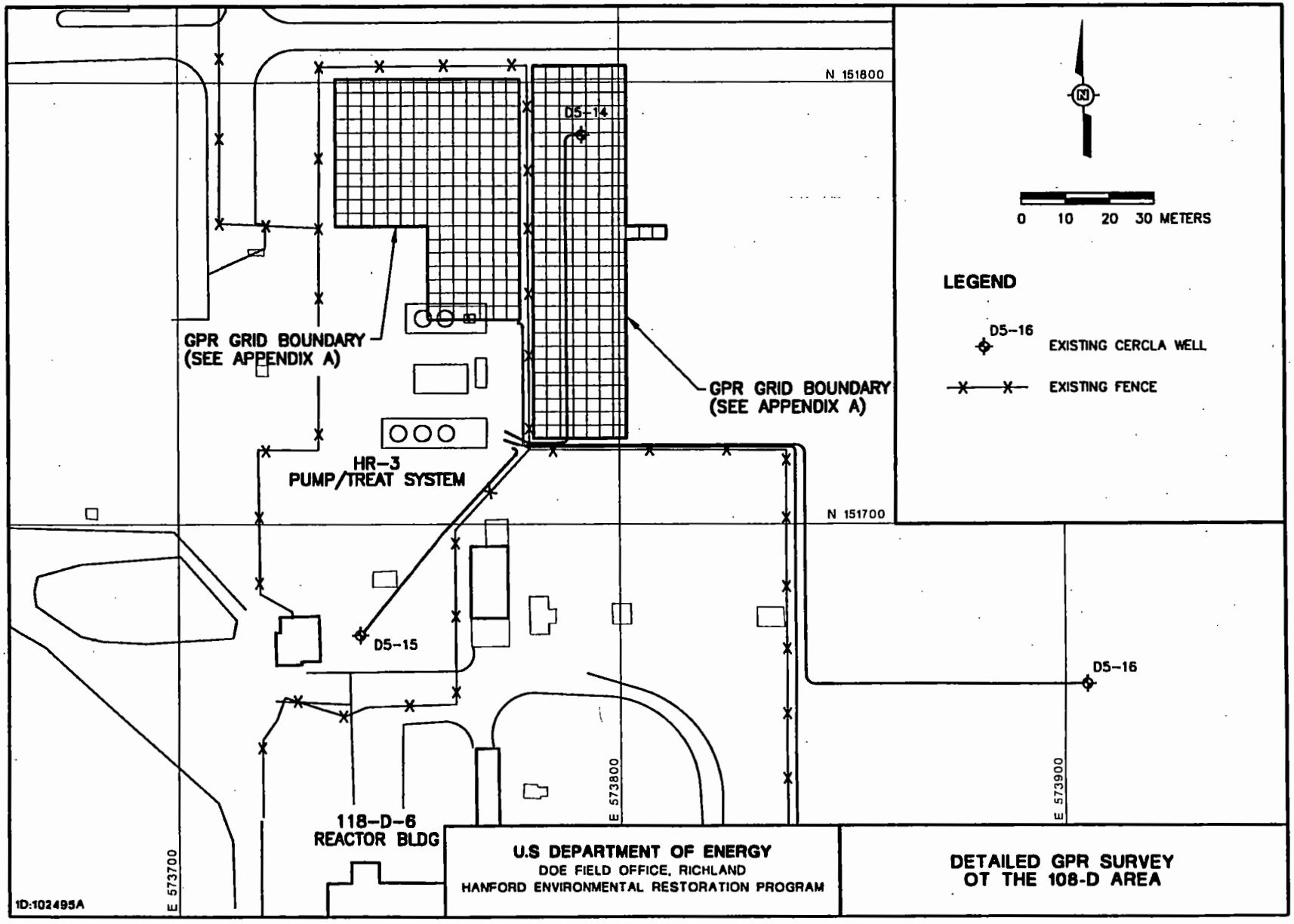

Figure 8. 100-D/DR Area.

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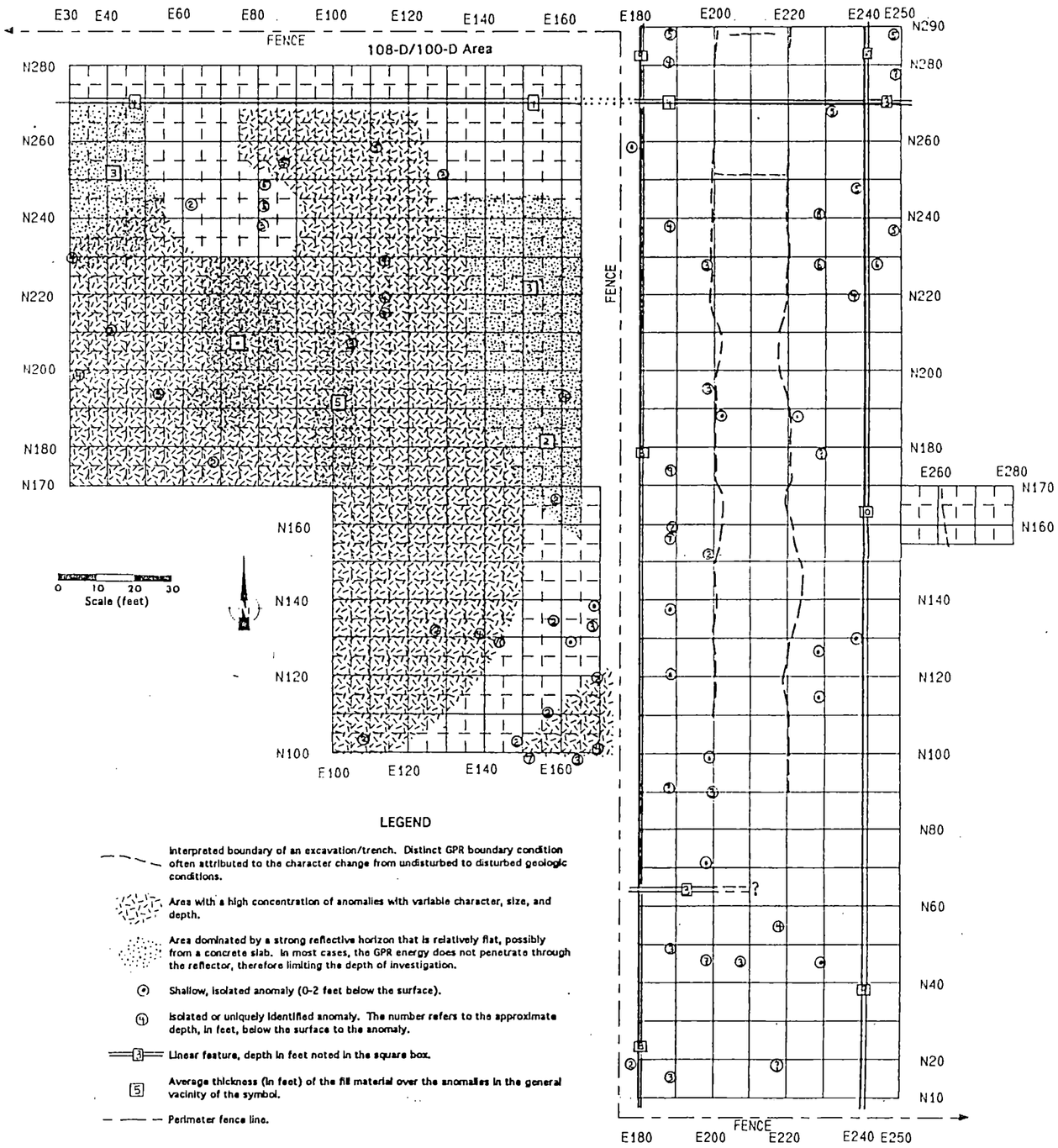
APPENDIX A

GROUND PENETRATING RADAR

9613470.0991



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