SGW-38338
Revision 0

Remedial Process Optimization for the 100-D Area Technical Memorandum Document

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Project Hanford Management Contractor for the
U.S. Department of Energy under Contract DE-AC06-96RL13200

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Richland, Washington

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D. J. Shrimpton
Fluor Hanford, Inc.

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EXECUTIVE SUMMARY

The 100-D Area has received, and will continue to receive, focused attention from the U.S. Department of Energy and stakeholders for reasons that include the following:

- Recently discovered "hot spots" (high-concentration areas) in both the vadose zone and groundwater.
- Groundwater monitoring results that suggest continued discharge of groundwater to the Columbia River with hexavalent chromium concentrations >20 μg/L. This potential impact to the river indicates the need to enhance, modify, or supplement the interim remedial actions that have been in place since 1997.
- Groundwater monitoring suggesting that the mass of hexavalent chromium in the plume has not decreased substantially over the past 10 years. These results suggest that alternative approaches to enhance, modify, or supplement the existing interim actions are necessary to achieve cleanup goals and protect the river.

To address these issues, three sets of actions for the 100-D Area are being considered:

1. Actions that will address the hot spot areas as quickly as possible. The objective of these actions will be to remove a significant portion of the contaminant mass from the vadose zone hot spot(s) contributing to the groundwater plume(s). Additionally, actions will be taken to optimize current pump-and-treat remedial activities to improve performance and address regulatory concerns. These actions can be considered near-term actions.
2. Actions that will protect the river by 2012. Actions taken to protect the river can be considered short-term actions.
3. Actions that will result in achieving substantial cleanup of the hexavalent chromium plume by 2020. Such actions again include optimization of current pump-and-treat remedial activities and may also include new remedial actions as appropriate. Actions taken to achieve plume cleanup can be considered long-term actions.

Remediation process optimization (RPO) efforts are underway at the 100-D Area to assist with addressing these issues. In particular, the RPO efforts have focused on addressing protection of

the river and achieving plume cleanup. The efforts have also looked at reducing cost and improving the performance of the existing systems. This technical memorandum reports on five of the seven RPO tasks, as follows:

- Reviewed and summarized the conceptual site model (CSM) and discussed implications for site remediation.
- Reviewed the design and performance of the existing 100-D Area ex situ remedial systems and treatability actions; identified system or process modifications to improve performance.
- Identified and screened in situ and ex situ remedial technologies with the potential to improve remedial performance at the site.
- Developed and summarized potential remedial action alternatives (RAAs) for the site based on the screened technologies.
- Developed pre-conceptual designs and costs for three pump-and-treat technologies that were identified during the screening process as candidates for inclusion into one or more of the proposed RAAs.

The two remaining RPO tasks will be completed after this document has been accepted by the U.S. Department of Energy, Richland Operations Office (RL) and will be documented in subsequent documents within the first quarter of fiscal year 2009 (FY09). The tasks remaining to be completed are listed below:

- Develop pre-conceptual level designs and costs for the RAAs and screen the RAAs using appropriate decision analysis tools that incorporate the *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* criteria for evaluation. A decision analysis workshop will be held to screen the RAAs. These results will be included in a final document that will describe the overall remedial approach that is recommended for the 100-D Area.
- Develop a process and control optimization plan for the iterative and continuing optimization of the existing and potential future 100-D Area pump-and-treat systems.

- Perform pilot testing of some of the components of the preferred RAAs, as necessary. It is currently envisioned that any pilot testing would be implemented as soon as possible in order to enable full-scale implementation of some of the components in FY09/FY10.

These activities will also be closely integrated with other ongoing activities including the following:

- Actions that will address the hot spots (e.g., near the old sodium dichromate transfer station and other areas where sodium dichromate product was handled). The objective of these actions will be to remove a significant portion of the contaminant mass from the vadose zone hot spot(s) that are contributing to the groundwater plume(s). These near-term actions are likely to be implemented in FY09/FY10.

- The remedial investigation/feasibility study (RI/FS) process. Currently, an integrated RI work plan is being developed for 100-D Area RI/FS activities. This process will lead to a final Record of Decision (ROD) for the site.

E1.0 REVIEW CONCEPTUAL SITE MODEL

Key features of the CSM for the 100-D Area are as follows:

- Simplistically, the site geology is composed of very coarse sands and gravel (including cobbles), but there are some stringers of silts and sands.

- The average depth of groundwater is 24 m (80 ft) below ground surface; therefore, the vadose zone is relatively thick.

- The Columbia River stage has a significant impact on groundwater levels and flow paths. During parts of the year, the river stage is higher than adjacent groundwater elevations.

- Widespread discharge and leaks of cooling water containing approximately 2 mg/L of hexavalent chromium, and mounding of groundwater during operations, resulted in a widespread hexavalent chromium plume at or below this concentration.

- More localized releases of concentrated chromate solutions resulted in higher concentration hot spots in some of the areas where these more concentrated solutions

were historically handled or transported. Hot spots include high concentrations of hexavalent chromium in porewater in the vadose zone. These hot spots in the vadose zone and saturated zone likely serve as continued sources of contamination to the groundwater plume. Not all of these hot spots have been identified, and it may be very challenging to identify all of them.

- The hexavalent chromium plume is divided by a groundwater mound into a northern plume and a southern plume as a result of water leaks from the 182-D reservoir.
- Groundwater with hexavalent chromium concentrations >20 μg/L currently exists in monitoring wells close to the river and likely discharges to the river during part of the year at concentrations greater than 20 μg/L.
- These concentrations exist despite the interim remediation systems that have been in operations for over 10 years. Although the interim remediation systems were not designed to address the entire plume, the persistence of the plume may support the conclusion that there are ongoing primary and/or secondary sources of hexavalent chromium contamination. Enhanced, modified, or supplemental remedial actions may be necessary to address the above-mentioned issues.

E2.0 REVIEW OF CURRENT EX SITU TREATMENT SYSTEMS AND OPTIMIZATION STUDIES

The design and operational processes of the 100-HR-3 and the DR-5 treatment systems were reviewed, and actions to optimize the performance and reduce operational costs were identified. The results of an electrocoagulation pilot test study were also evaluated to determine whether this technology should be considered as an alternative to ion exchange (IX) at the 100-D Area.

Both the 100-HR-3 and the DR-5 treatment systems have performed well in terms of total system availability, hexavalent chromium removal efficiencies, and effluent hexavalent chromium concentrations. However, operation and maintenance (O&M) costs could be reduced by optimizing these systems. A number of recommendations were developed to optimize the operations of each system. Electrocoagulation pilot testing showed that this technology was able to reduce hexavalent chromium concentrations to <20 μg/L, but only when electrodes

were clean. Keeping electrodes clean was a significant challenge and in addition, the electrocoagulation unit was unable to operate unattended. A number of operational suggestions were made in the event that electrocoagulation is to be pursued further.

E3.0 TECHNOLOGY EXCHANGE MEETING

A hexavalent chromium treatment technology exchange meeting was initiated so RL and Fluor Hanford, Inc. staff could obtain information regarding full-scale remediation of hexavalent chromium-contaminated groundwater. The presenters and meeting attendees generally agreed that the optimization of the current pump-and-treat systems and/or incorporation of new IX media or treatment technologies may provide cost and performance benefits. However, there was also a general consensus that treatment of the hexavalent chromium plume in the 100-D Area with the In Situ Redox Manipulation treatment zone and pump-and-treat technology alone would require long periods of time to achieve remedial action objectives (RAOs). To accelerate remediation, a more aggressive approach that potentially uses both ex situ and in situ technologies to address both the groundwater and the vadose zone was recommended. There was particular interest in the in situ reduction of hexavalent chromium accomplished using either chemical or biological approaches, or a combination thereof. Whichever approach or combination of approaches is ultimately implemented, it was recognized that it will be important to achieve and maintain hydraulic control of in situ treatment areas to ensure protection of the Columbia River and to avoid potential impacts (e.g., bio-fouling) to the pump-and-treat systems that are currently in place.

E4.0 TECHNOLOGY SCREENING AND DECISION ANALYSIS

A technology screening meeting was held to identify remedial technologies having the potential to accelerate remediation of the 100-D Area. The meeting involved (1) identifying working RAOs that may be formalized in the final ROD for the 100-D Area, (2) formulating technology screening criteria to be used to rank the technologies, (3) brainstorming to create a list of potential technologies, (4) screening the potential technologies against the screening criteria, and (5) combining high scoring technologies into RAAs that could potentially achieve 100-D Area RAOs. The results of screening are as follows:

- The top-scoring river protection technologies were biological barrier, followed by hydraulic barriers at the river, sparging wells, and chemical barrier.
- Top-scoring vadose zone treatment technologies were biological infiltration, followed by chemical infiltration, remove/treat/dispose, and water flushing.
- Top-scoring groundwater treatment technologies were in situ biological treatment, followed by in situ chemical treatment, in situ biological barrier, and in situ chemical barrier.
- Top-scoring ex situ groundwater treatment technologies were optimize existing systems, followed by extraction of groundwater and re-infiltration with biological amendments, ferrous iron reduction, and continue all actions (keep using IX as in the past).

E5.0 PRE-CONCEPTUAL DESIGN AND COSTS FOR EX SITU GROUNDWATER TREATMENT TECHNOLOGIES

RL is considering upgrading or replacing the existing ex situ treatment systems for the 100-D Area as part of the ongoing RPO effort. Design criteria and pre-conceptual designs and cost estimates were presented for three ex situ treatment approaches that may be able to treat groundwater more cost effectively than the current systems. These three ex situ technologies are (1) IX with offsite regeneration, (2) IX with onsite regeneration, and (3) ferrous chloride treatment.

All three technologies will remove hexavalent chromium from the groundwater and meet water quality criteria for the treated water. The estimated capital costs of all three technologies were very similar, despite differences among the processes. Estimated O&M cost was the most significant differentiator. The technology with the lowest estimated O&M cost is IX with onsite regeneration, followed by the ferrous chloride process (with estimated O&M costs approximately 20% higher). The largest solid waste stream is generated by the ferrous chloride process, and the smallest solid waste stream is generated by IX with offsite regeneration.

The process of IX with onsite regeneration uses the least well-established approach to managing spent regenerant brine and poses some technical risk that may be addressed by testing and evaluation. The main uncertainties associated with this process are rates and optimum process

conditions for hexavalent chromium reduction, and the rate and completeness of ferrous iron oxidation, to prevent injection well fouling by such high ionic-strength solutions. The ferrous chloride process is a proven technology that is less technically challenging relative to IX with onsite regeneration. Site-specific testing of IX with onsite regeneration and ferrous chloride treatment is recommended.

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LISTOF TERMS

bgs	below ground surface
CERCLA	*Comprehensive Environmental Response, Compensation, and Liability Act of 1980*
CSM	conceptual site model
CY	calendar year
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
ERDF	Environmental Restoration Disposal Facility
FH	Fluor Hanford, Inc.
FS	feasibility study
FY	fiscal year
gpm	gallons per minute
HDPE	high-density polyethylene
ISRM	In Situ Redox Manipulation
IX	ion exchange
MCL	maximum contaminant level
MNA	monitored natural attenuation
N/A	not applicable
O&M	operation and maintenance
psi	pounds per square inch
psid	pounds per square inch differential
RAA	remedial action alternative
RAO	remedial action objective
RI	remedial investigation
RL	U.S. Department of Energy, Richland Operations Office
ROD	Record of Decision
RPO	remediation process optimization
TCLP	toxicity characteristic leaching procedure

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METRIC CONVERSION CHART

Into Metric Units			Out of Metric Units		
If You Know	*Multiply By*	*To Get*	*If You Know*	*Multiply By*	*To Get*
Length			**Length**		
inches	25.4	millimeters	millimeters	0.039	inches
inches	2.54	centimeters	centimeters	0.394	inches
feet	0.305	meters	meters	3.281	feet
yards	0.914	meters	meters	1.094	yards
miles	1.609	kilometers	kilometers	0.621	miles
Area			**Area**		
sq. inches	6.452	sq. centimeters	sq. centimeters	0.155	sq. inches
sq. feet	0.093	sq. meters	sq. meters	10.76	sq. feet
sq. yards	0.836	sq. meters	sq. meters	1.196	sq. yards
sq. miles	2.6	sq. kilometers	sq. kilometers	0.4	sq. miles
acres	0.405	hectares	hectares	2.47	acres
Mass (weight)			**Mass (weight)**		
ounces	28.35	grams	grams	0.035	ounces
pounds	0.454	kilograms	kilograms	2.205	pounds
ton	0.907	metric ton	metric ton	1.102	ton
Volume			**Volume**		
teaspoons	5	milliliters	milliliters	0.033	fluid ounces
tablespoons	15	milliliters	liters	2.1	pints
fluid ounces	30	milliliters	liters	1.057	quarts
cups	0.24	liters	liters	0.264	gallons
pints	0.47	liters	cubic meters	35.315	cubic feet
quarts	0.95	liters	cubic meters	1.308	cubic yards
gallons	3.8	liters			
cubic feet	0.028	cubic meters			
cubic yards	0.765	cubic meters			
Temperature			**Temperature**		
Fahrenheit	subtract 32, then multiply by 5/9	Celsius	Celsius	multiply by 9/5, then add 32	Fahrenheit
Radioactivity			**Radioactivity**		
picocuries	37	millibecquerels	millibecquerels	0.027	picocuries

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1.0 INTRODUCTION

The 100-D Area has received, and will continue to receive, focused attention from the U.S. Department of Energy (DOE) and stakeholders for reasons that include the following:

- Recently discovered "hot spots" (high-concentration areas) in both the vadose zone and groundwater.
- Groundwater monitoring results that suggest continued discharge of groundwater to the Columbia River with hexavalent chromium concentrations >20 μg/L. This potential impact to the river indicates the need to enhance, modify, or supplement the interim remedial actions that have been in place since 1997.
- Groundwater monitoring results that suggest that the mass of hexavalent chromium in the plume has not decreased substantially over the past 10 years. Recent groundwater characterization efforts identified higher-than-anticipated hexavalent chromium concentrations upgradient of existing groundwater interim remedial actions. In addition, recent source area surface remediation efforts have identified areas of vadose zone contamination in close proximity to the groundwater plume location. These recent discoveries indicate that alternative approaches to enhance, modify, or supplement the existing interim actions are necessary to achieve cleanup goals and protect the river.

To address these issues, three sets of actions for the 100-D Area are being considered:

1. Actions that will address the hot spot areas (e.g., near the old sodium dichromate transfer station and other areas where sodium dichromate product was handled) as quickly as possible. The objective of these actions will be to remove a significant portion of the contaminant mass from the vadose zone hot spot(s) contributing to the groundwater plume(s). Additionally, actions will be taken to optimize current pump-and-treat remedial activities to improve performance and address regulatory concerns. These actions can be considered near-term actions.
2. Actions that will protect the river by 2012. Actions taken to protect the river can be considered short-term actions.
3. Actions that will result in achieving substantial cleanup of the hexavalent chromium plume by 2020. Such actions again include optimization of current pump-and-treat remedial activities, and may also include new remedial actions as appropriate. Actions taken to achieve plume cleanup can be considered long-term actions.

In fiscal year 2008 (FY08), a Fluor Hanford, Inc. (FH) team began remediation process optimization (RPO) of the interim remedial actions at the 100-D Area. The RPO process is the systematic evaluation and enhancement of site remediation processes to foster the achievement of the remedial action objectives (RAOs) for the site with improved performance and reduced cost. The RPO also involves optimization of the remedial strategy by re-evaluating the overall approach and formulating, if applicable, remedial action alternatives (RAAs) that have a higher likelihood of achieving RAOs at reduced cost.

At the 100-D Area, the RPO efforts have focused on addressing protection of the river and achieving plume cleanup, as well as reducing the cost and improving the performance of the existing systems. Addressing the hot spot areas is being addressed by a separate effort, but one that is being closely coordinated with the RPO effort.

In addition to these efforts, FH is undertaking a parallel remedial investigation/feasibility study (RI/FS) process. Currently, an integrated RI work plan is being developed for 100-D Area RI/FS activities. These activities are occurring concurrently with the RPO activity and will ultimately result in a final Record of Decision (ROD). The RI/FS activities are being closely integrated with these RPO activities.

To accomplish the 100-D Area RPO effort, seven tasks were originally identified. Five of those tasks have been completed, the results of which are presented in this document. The completed RPO tasks include the following:

- Review and summarize the conceptual site model (CSM) and discuss implications for site remediation.
- Review the design and performance of the existing 100-D Area ex situ remedial systems and treatability actions; identify system or process modifications to improve performance.
- Identify and screen in situ and ex situ remedial technologies with the potential to improve remedial performance at the site.
- Use the preferred technologies to develop a range of potential RAAs for the site. The RAAs specifically address both protection of the river and plume remediation.
- Develop pre-conceptual designs and costs for three pump-and-treat technologies that were identified during the screening process as candidates for inclusion into one or more of the proposed RAAs.

The two remaining RPO tasks will be completed after this document has been accepted by the U.S. Department of Energy, Richland Operations Office (RL) and will be documented in subsequent documents within the first quarter of FY09. The tasks remaining to be completed are described below:

- Develop pre-conceptual level designs and costs for the RAAs and screen the RAAs using appropriate decision analysis tools that incorporate the *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* (CERCLA) criteria for evaluation. These results will be included in a final document that will describe the overall remedial approach that is recommended for the 100-D Area.
- Develop a process and control optimization plan for the iterative and continuing optimization of the existing and potential future 100-D Area pump-and-treat systems.
- Pilot testing of some of the components of the preferred alternatives may be necessary. It is currently envisioned that any pilot testing would be implemented as soon as possible in order to enable full-scale implementation of some of the components in FY09/FY10.

1.1 REPORT ORGANIZATION

This document consists of eight sections and five appendices. In addition to the introduction, the results of specific tasks conducted as part of the 100-D Area RPO are presented in this document as follows:

- Section 2.0: Presents a review of the 100-D Area CSM.
- Section 3.0: Evaluates the performance and operation of the ex situ treatment systems that are in use, or that have been tested, at the 100-D Area.
- Section 4.0: Summarizes the results of the hexavalent chromium treatment technology exchange meeting conducted in April 2008 to facilitate the identification of promising remedial technologies.
- Section 5.0: Summarizes the results of a technology screening and decision analysis meeting.
- Section 6.0: Summarizes the pre-conceptual designs and cost estimates for three pump-and-treat technologies.
- Section 7.0: Summarizes the conclusions and recommendations.
- Section 8.0: Provides the references cited in this Technical Memorandum.
- Appendix A: Provides the proposed remedial action alternatives.
- Appendix B: Provides a list of the technology screening meeting attendees.
- Appendix C: Includes the sensitivity analysis of the decision scoring weights.
- Appendix D: Provides the modified groundwater capital cost factors for aboveground facilities.
- Appendix E: Includes the capital and operation and maintenance (O&M) cost breakdown tables.

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2.0 OVERVIEW OF THE 100-D AREA CONCEPTUAL SITE MODEL

Section 2.0 presents a review of the CSM for the 100-D Area. A detailed understanding of the CSM, including uncertainties and data gaps, is an important component of any successful RPO effort. This understanding is facilitated by the integration of a range of site-specific data and other information (e.g., process history, geology, hydrology, geochemistry, and impacts of ongoing remedies) into a coherent CSM. The information presented in this section has been gleaned, summarized, and synthesized from a wide range of published and unpublished data including, but not limited to, information from 100-HR-3 annual reports, previous CSM reviews, existing and ongoing laboratory and field-based investigations, web sites, and discussions with technical personnel involved in the investigations. This overview is believed to present an accurate summary of the current status of the CSM for the 100-D Area that is suitable for facilitating the selection and evaluation of appropriate remedial technologies and RAAs for this site. This effort has been coordinated with other ongoing systematic planning efforts within the 100-D Area.

The primary objectives of this section are as follows:

1. Present an overview of the 100-D Area CSM based on the results of previous and, where possible, ongoing characterization and remediation efforts for the 100-D Area.
2. Identify key data gaps and uncertainties in the CSM and integrate with the RI work plan.
3. Facilitate subsequent identification of potential future remedial actions for the 100-D Area.

Pursuant to these objectives, the following information is presented:

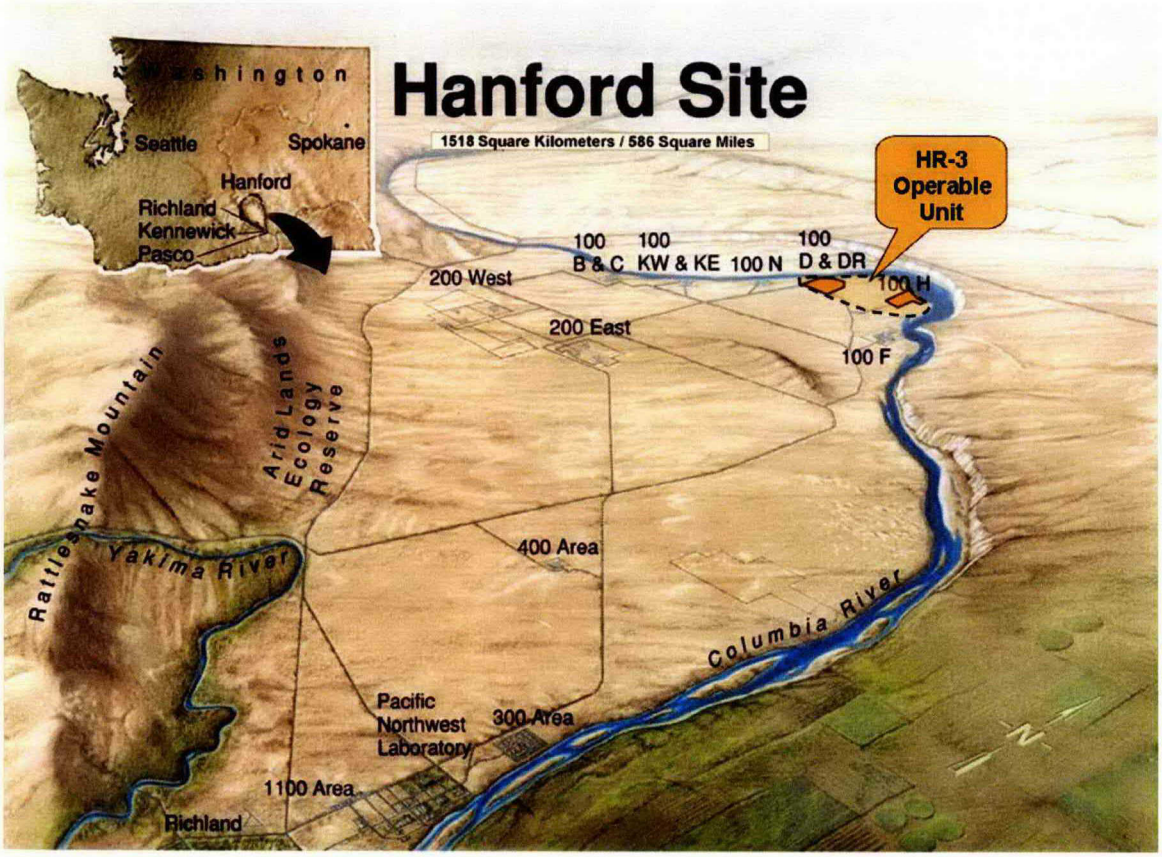
- Site setting
- Geologic setting
- Site hydrology
- Historical site operations and potential sources of contamination
- Nature and extent of hexavalent chromium contamination
- Implications for current and potential future remedial actions
- Conclusions and recommendations.

2.1 SITE SETTING

The Hanford 100-D Area is part of the 100-HR-3 Groundwater Operable Unit, located adjacent to the Columbia River in the northeast corner of the Hanford Site in southeastern Washington State (Figure 2-1). The 100-D Area encompasses the operating areas of two former DOE production reactors (the former D and DR Reactors). While these reactors were operational, large volumes of river water were treated with sodium dichromate (to inhibit corrosion of the reactor piping) and used as a coolant for the reactors. After a single pass through the reactor and before being discharged back to the river, the coolant water was sent to unlined retention basins to cool and so the short-lived radioactive contaminants would decay. This approach to reactor cooling led to the introduction of large volumes of process water contaminated with low concentrations of hexavalent chromium into the vadose zone, and ultimately into the groundwater aquifer and adjacent Columbia River. In addition, numerous leaks and spills of

concentrated sodium dichromate stock solution over the lifetime of reactor operations led to higher concentrations of chromate in the vadose zone and groundwater in localized areas.

Figure 2-1. Hanford Site Showing the Location of the 100-D Area Within the 100-HR-3 Operable Unit.

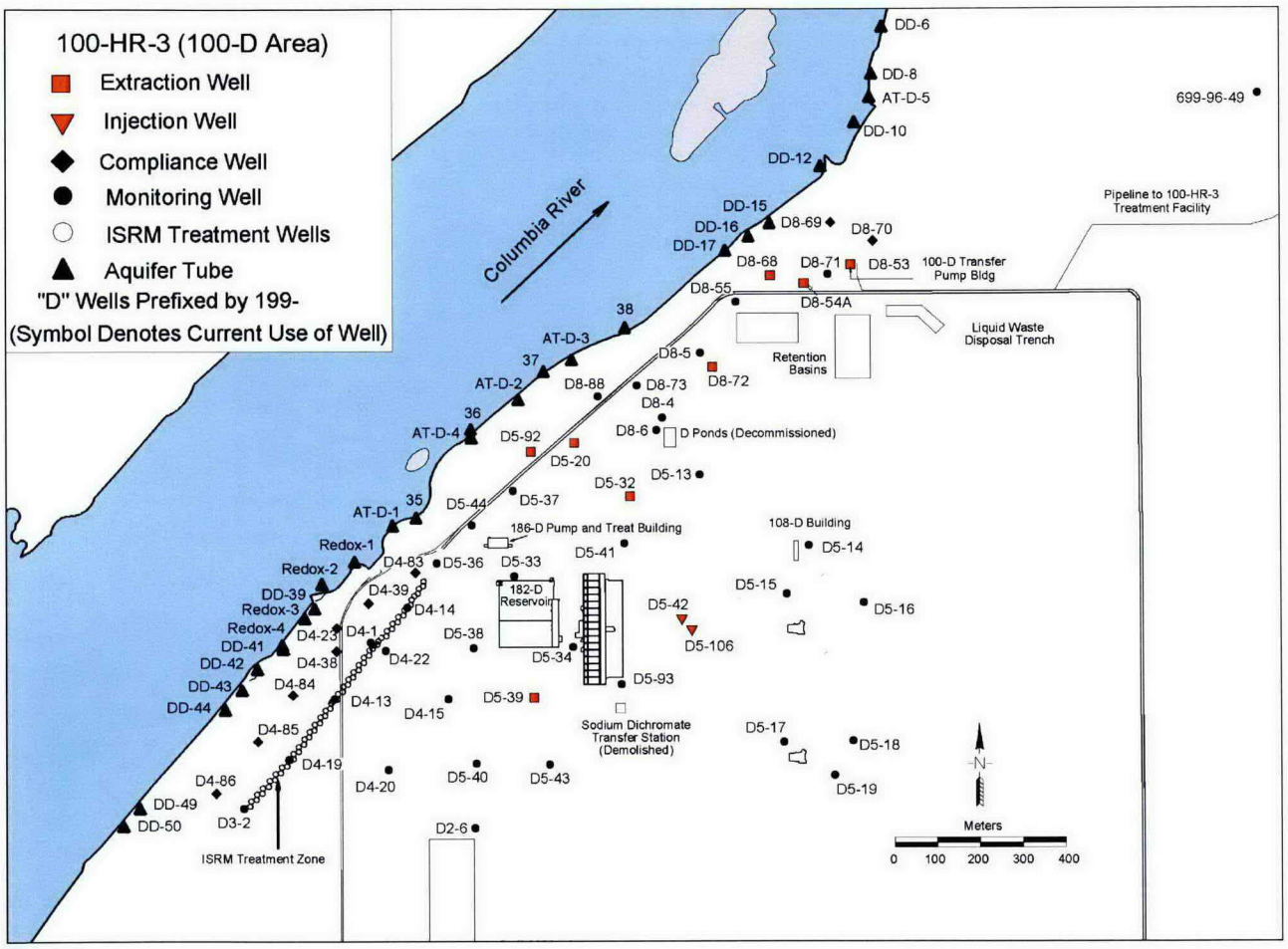


The presence of groundwater contaminated with hexavalent chromium and other selected constituents (see Section 2.5) and the ongoing discharge of this contaminated groundwater to the Columbia River are an unfortunate and problematic legacy of the historical activities at this site. In order to mitigate the impacts of contamination at the 100-D Area (and other related sites) to human health and the environment, both in situ and ex situ remedial actions have been implemented in an attempt to achieve the following RAOs specified in the *Declaration of the Record of Decision for the 100-HR-3 and 100-KR-4 Operable Units at the Hanford Site (Interim Remedial Action)* (EPA et al. 1996):

- RAO #1: Protect aquatic receptors in the river bottom substrate from contaminants in groundwater entering the Columbia River.
- RAO #2: Protect human health by preventing exposure to contaminants in the groundwater.
- RAO #3: Provide information that will lead to the final remedy.

Interim remedial actions for the 100-D Area were initiated in 1997 when a pump-and-treat system was installed to reduce the levels of hexavalent chromium in groundwater discharging to the river. This initial treatment system (hereinafter denoted as the 100-HR-3 system) extracts contaminated groundwater using four extraction wells (199-D8-53, 199-D8-54A, 199-D8-68, and 199-D8-72) located in the northeastern part of the 100-D Area (Figure 2-2). The extracted groundwater is piped to the treatment plant in the 100-H Area where it is treated by ion exchange (IX) and is then reinjected into the aquifer.

Figure 2-2. 100-D Area Treatment System Infrastructure.



Between 2000 and 2003, the 100-HR-3 system was augmented by the phased installation of a passive treatment system known as the In Situ Redox Manipulation (ISRM) treatment zone (Figure 2-2). The ISRM treatment zone was created by the injection of a strong reducing agent (sodium dithionite) into the aquifer between the river and the southern lobe of the 100-D Area hexavalent chromium plume (hereinafter denoted as the southern plume). The objective of the ISRM was to form a reactive barrier that would substantially reduce the levels of hexavalent chromium discharging to the river in this part of the 100-D Area. At the time of implementation, the degree of contamination upgradient of the ISRM barrier was unknown. Augmentation of the ISRM barrier is being considered as the degree of upgradient hexavalent chromium contamination has been shown to be greater than previously understood.

Active treatment of the 100-D Area was expanded in 2004 with the addition of a second IX pump-and-treat system (hereinafter denoted as the DR-5 system). The DR-5 system was designed to capture hexavalent chromium contamination that is located further south in the 100-D Area plume (and upgradient of the ISRM). The extraction wells currently operating as part of the DR-5 system are 199-D5-20, 199-D5-32, 199-D5-39, and 199-D5-92 (Figure 2-2).

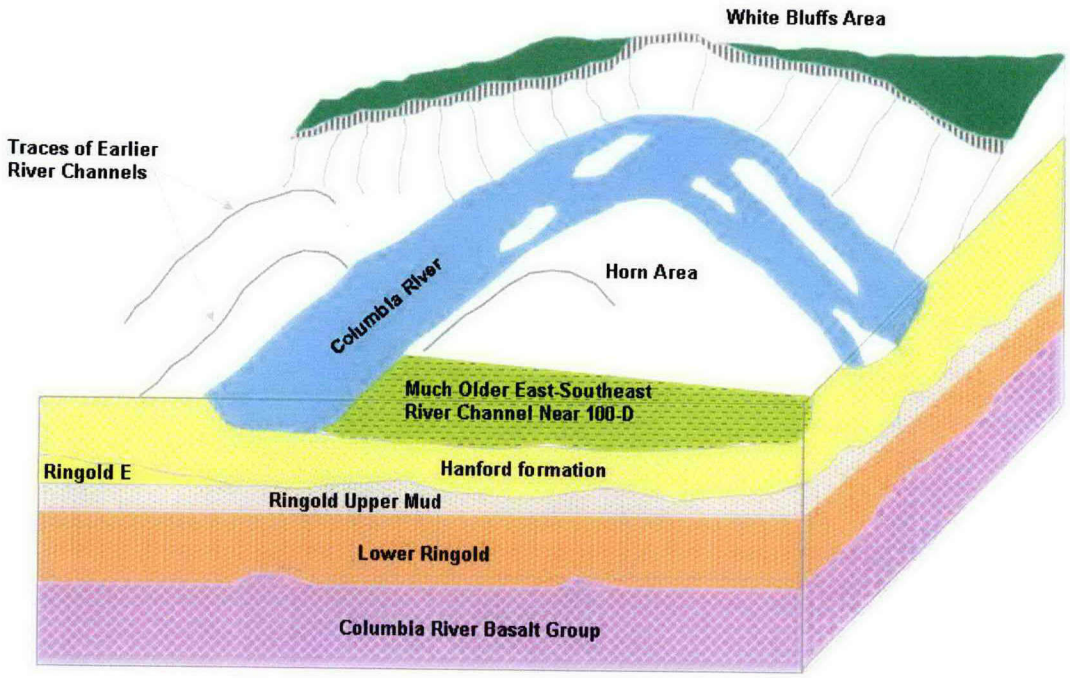
Despite the natural flushing of the aquifer that has occurred since the reactors were taken off-line and the installation and operation of the 100-D Area treatment systems, elevated concentrations of hexavalent chromium have persisted in the groundwater at the 100-D Area (including some areas downgradient of the ISRM). The persistence of the plume over time and the elevated concentrations provide some evidence that a substantial residual source of hexavalent chromium continues to reside in the vadose zone (and possibly in abandoned infrastructure) at this site. These residual sources are expected to continue to feed the 100-D Area groundwater plumes with additional hexavalent chromium for the foreseeable future until vadose zone remedial actions currently under development are implemented. Both historical and recent monitoring activities indicate that the RAOs for the 100-D Area have not been achieved. The geologic setting of the 100-D Area and vicinity is discussed below.

2.2 GEOLOGIC SETTING

The Columbia River Basalts were extremely thick flows that covered an approximately 207,000 km^2 (80,000 mi^2) section of eastern Washington, Idaho, and Oregon about 6 to 16 million years ago. Subsequent to cooling, these basaltic units locally subsided, forming large broad basins such as the Pasco Basin, one of several sub-basins within the larger Columbia Basin. The Hanford Site is located within and covers about half of the Pasco Basin. The Columbia River bisects the Pasco Basin and it, or its ancestor, deposited the upper Miocene/ lower Pliocene Ringold Formation between 1.8 to 5 million years ago. Various fluvial, glacio-fluvio, and aeolian units were deposited after the Ringold Formation. Multiple periods of glaciation affected the region and episodes of glacial advance and retreat continued until about 12,000 years ago. The Missoula floods occurred between about 12,000 and 15,000 years ago and were the final large-scale flood events affecting the Pasco Basin (including the Hanford area) and resulted in the deposition of the Hanford formation. Since cessation of the final major flooding events and a return to normal river volume flows over the last 12,000 years, the region has been receiving alluvium, talus, and landslide deposits. The remaining soils and sediments form the rolling hills and farmland of eastern Washington as seen today. Surface features that reflect the catastrophic Missoula floods in the area include giant ripple marks and gravel bars.

The geology of the 100-D Area is consistent with the regional geological setting and the processes described above. The two main sedimentary units in the 100-D Area are the Pleistocene Hanford formation and the underlying Ringold Formation (Figures 2-3 and 2-4). The existing river system has a moderate flow with relatively straight stretches except where the river is deflected at a high angle (forming the Horn area) in the vicinity of the White Bluffs area (Figure 2-3). Well-defined curvilinear channel trace features are visible on both sides of the existing river, indicating that the river channel has repeatedly migrated across the valley floor.

Figure 2-3. Conceptual Illustration of the Geologic Setting of the Horn Area.

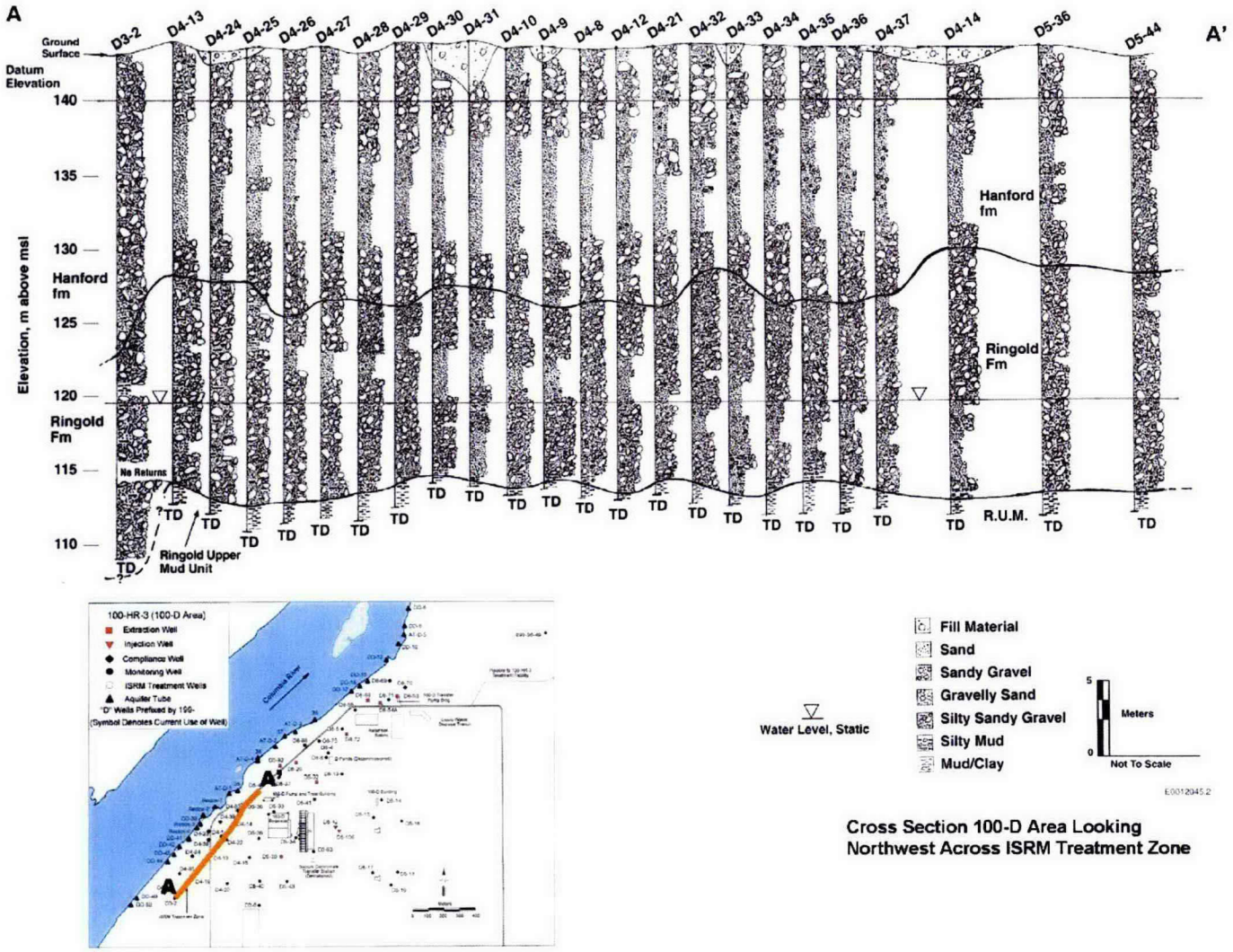


2.2.1 Hanford Formation

The Hanford formation constitutes the majority of the vadose zone in the 100-D Area (Figure 2-4), and it is characterized by large to very large felsic (granite, quartzite, gneiss, and schist) to mafic (basalt and andesite) cobble-boulder fragments/clasts in open-framework gravel and sand with little to no silt and clay. Discrete lenses of sand are present within the Hanford Site at the 100-D Area and may represent small channel scours and isolated overbank deposits produced by late-stage glacial flooding or Columbia River flooding. These relatively small and isolated pockets or lenses of sand may form preferential flow paths or collection zones for contaminants released into the vadose zone (see Section 2.3 for discussion of vadose zone releases).

The color of the Hanford formation is variegated and ranges from tan and brown to gray and black and blends of those colors. Geologic logs from recent borings within the 100-D Area describe a substantial basaltic gravel and sand content. Geologic descriptions indicate up to 85% basaltic material, which is exceedingly high for any sediment ascribed to the Hanford formation. Reportedly, the basalt content decreases with depth, suggesting that the upper (basalt-rich) part of the Hanford formation in this area was reworked during post-depositional Columbia River flood events. Near the contact with the underlying Ringold Formation, the basalt content of the Hanford formation reportedly decreases to 20% to 30%, an amount more typical of the Hanford formation.

Figure 2-4. Geological Cross-Section Through a Portion of the 100-D Area.



2.2.2 Ringold Formation

The late stage catastrophic flooding that deposited the Hanford formation in the 100-D Area eroded the upper units of Ringold Formation, leaving the Ringold Unit E as the youngest unit of the Ringold Formation remaining in the 100-D Area. The remaining Ringold Formation in the 100-D Area is composed primarily of pebble-sized gravels and sands. The Ringold Formation is underlain by the fine-sand, silt and clay-rich overbank deposits of the Ringold Upper Mud Unit.

2.3 SITE HYDROLOGY

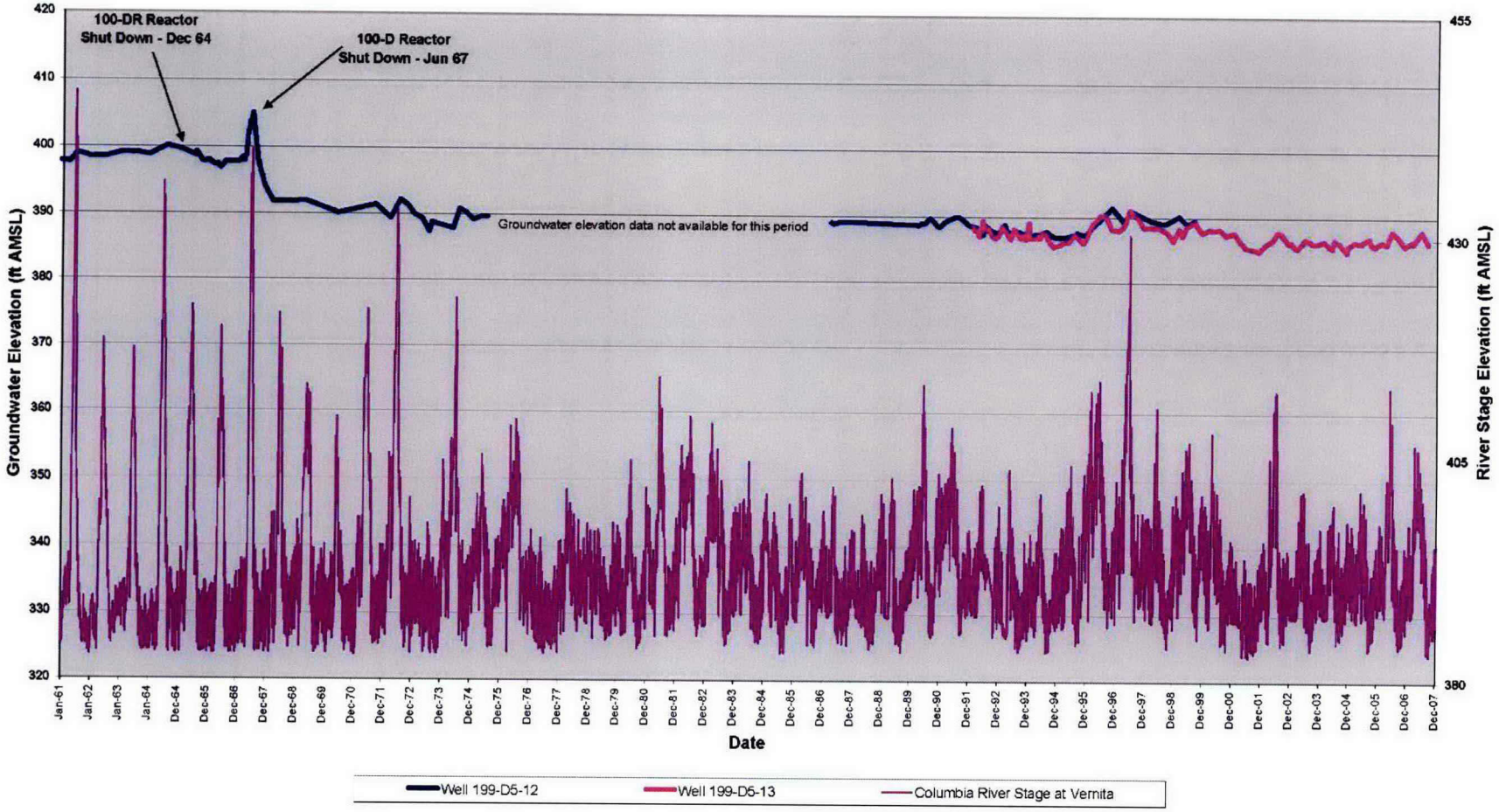
The vadose zone in the 100-D Area generally is composed of the Hanford formation. The aquifer system consists primarily of a shallow unconfined aquifer (typically supported by the Ringold Unit E) that is underlain by the Ringold Upper Mud. Although the Ringold Upper Mud is saturated, it has a much lower hydraulic conductivity and is generally considered to be the lower boundary for the shallow unconfined aquifer in the 100-D Area. Although the shallow unconfined aquifer is usually supported by the Ringold Unit E, there are sections of the 100-D Area where the catastrophic flooding events that deposited the Hanford formation eroded through most or all of the Ringold Unit E and, in some cases, cut channels into the underlying Ringold Upper Mud. In these areas, which include portions of the central 100-D Area, the Hanford formation extends deeper into the section and supports the shallow unconfined aquifer. Generally, the coarse-textured Hanford formation exhibits higher hydraulic conductivities than the Ringold Unit E, and these areas may represent preferential pathways for groundwater transport.

The nearby Columbia River is a discharge boundary for the aquifer system, and the aquifer is in direct communication with the river along the shoreline of the 100-D Area (*Zone of Interaction Between Hanford Site Groundwater and Adjacent Columbia River* [PNNL-13674]). Groundwater elevation, gradient, and flow velocity at the 100-D Area are very responsive to changes in stage of the Columbia River. Although the Hanford Reach of the Columbia River, including the section adjacent to the 100-D Area, is a free-flowing stream, the river stage is controlled by discharge from Priest Rapids Dam, located approximately 19 km (12 mi) upstream from the 100-D Area. The Columbia River discharge and resulting river stage at the Hanford Reach vary substantially on a seasonal basis and even on a daily and hourly basis, depending on the operation of Priest Rapids Dam.

2.3.1 Groundwater Levels

The average ground surface elevation in the 100-D Area is about 140 m (460 ft) above mean sea level, and groundwater is commonly encountered at an average depth of about 24 m (80 ft) below ground surface (bgs) (i.e., groundwater elevation of approximately 119 m [390 ft] above mean sea level) at most locations in the 100-D Area. The depth to groundwater is as shallow as 0 ft bgs in the river shore adjacent to the Columbia River, with the deeper groundwater encountered in the inland areas where the ground surface rises away from the river. Groundwater-level measurements in the 100-D Area over the last few years indicate that fluctuations by up to ±2 m (6 ft) occur on a seasonal basis. Part of the variation in groundwater levels is produced by seasonal changes in the stage of the adjacent Columbia River. Figure 2-5 presents a hydrograph of selected monitoring wells and the adjacent Columbia River.

Figure 2-5. Comparison of Groundwater Elevation in Two 100-D Area Wells to Columbia River Stage.

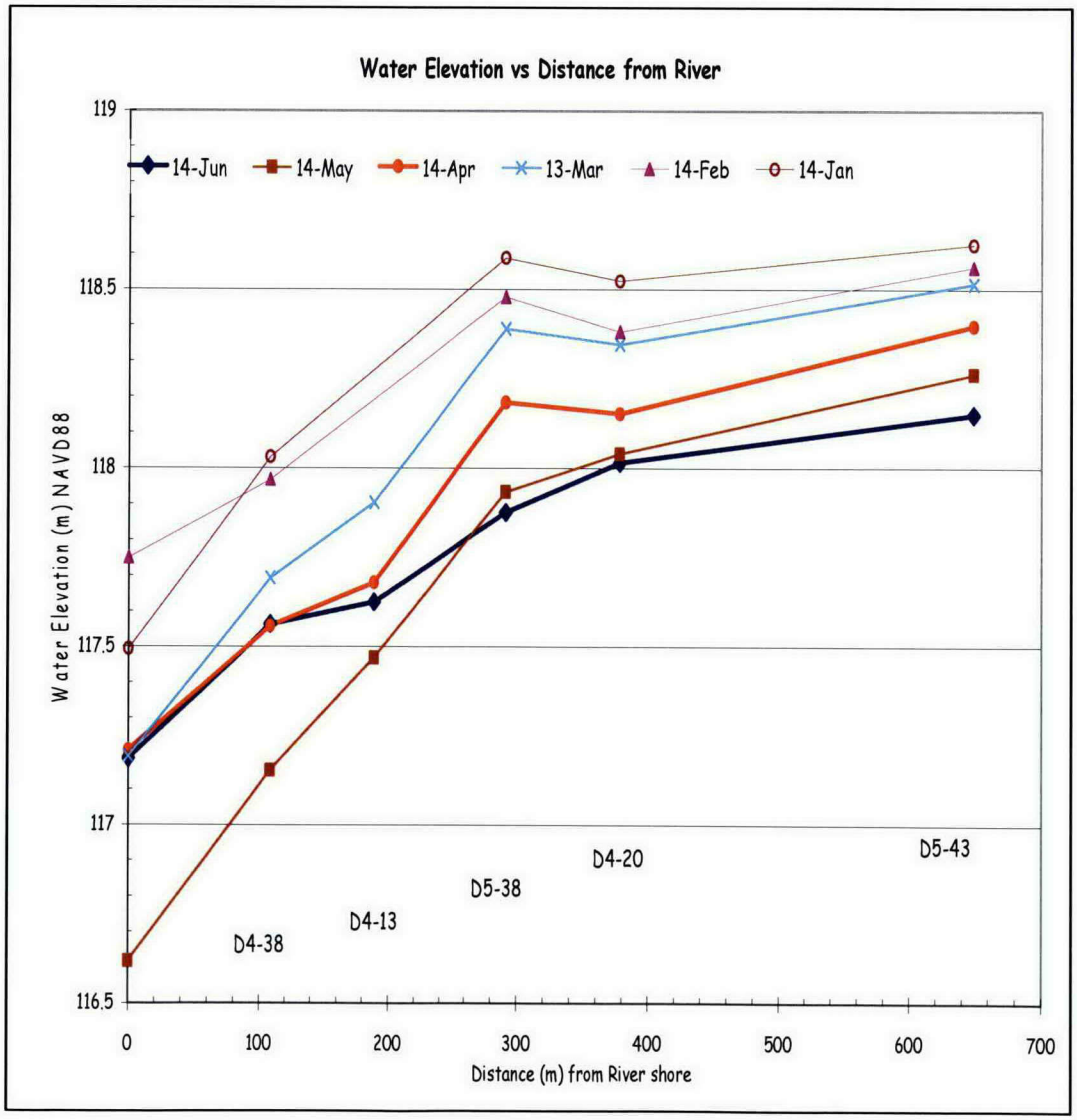


SOURCE: *Discharge and River Stage Data for the Columbia River Downstream of Priest Rapids Dam* from the U.S. Geological Survey's National Water Information System (NWIS) (USGS 2008).

Figure 2-5 also shows river elevations superimposed on the groundwater elevations from selected monitoring wells in the 100-D Area. Although the response of groundwater elevation to changes in the river stage is clearly visible, the effect on the aquifer decreases rapidly with distance from the river (Figure 2-6).

During operation of the D and DR Reactors (1944 through 1967), large intentional and unintentional releases of reactor cooling water created substantial groundwater mounding in the aquifer that varied in magnitude laterally and over time (*Ground Disposal of Reactor Coolant Effluent* [BNWL-CC-1352]). After the reactors were shut down, these mounding effects began to dissipate. In recent years, natural groundwater levels have been largely re-established over most of the 100-D Area, with the exception of the areas affected by local artificial extraction and recharge (e.g., the pump-and-treat extraction and injection wells, leakage from the 182-D reservoir, and episodic recharge from treatment of the ISRM wells).

Figure 2-6. Seasonal Changes in Groundwater Elevation of the Shallow Unconfined Aquifer in the 100-D Area as a Function of Distance from the Columbia River (1999 Data).



The 182-D reservoir is centrally located within the 100-D Area (Figure 2-2) and has been a source of groundwater mounding that has locally affected groundwater composition, flow direction, and flow velocity. Recent changes in operating practices at the reservoir (e.g., reducing the operating water level) have reduced the magnitude of the underlying mound. The effects of this mound on the nature and extent of the hexavalent chromium contamination are discussed in Section 2.4.

2.3.2 Flow Directions

Groundwater in the shallow unconfined aquifer beneath the 100-D Area flows generally west-northwest toward the Columbia River, which is a discharge boundary for the groundwater in the unconfined aquifer. The groundwater flow direction in the 100-D Area varies seasonally and laterally within the aquifer and appears to be affected by the following hydraulic features:

- Residual mounding of groundwater beneath the 182-D reservoir.
- Variations in the surface of the Ringold Upper Mud (e.g., paleo-channels) that create preferential pathways for groundwater flow, particularly during periods of low groundwater elevation.
- Variations in the river stage of the Columbia River, which can reverse flow direction (i.e., recharge from the river into the aquifer, or accumulation of bank storage) during periods of rapid and/or sustained rise in river stage. Transient groundwater flow reversal has been observed at locations as much as 152 m (500 ft) inland from the river shore.

Other locations at the 100-D Area may exhibit different directional variability because of their position relative to hydraulic activities (e.g., effects of extraction and reinjection of groundwater from the pump-and-treat system). As a result of these interactions and the effects of the river stage, the flow paths of groundwater (and consequently hexavalent chromium) discharging from the shallow unconfined aquifer to the river are believed to be complex. Nevertheless, the groundwater flow direction remains generally toward the Columbia River.

2.3.3 Flow Velocities

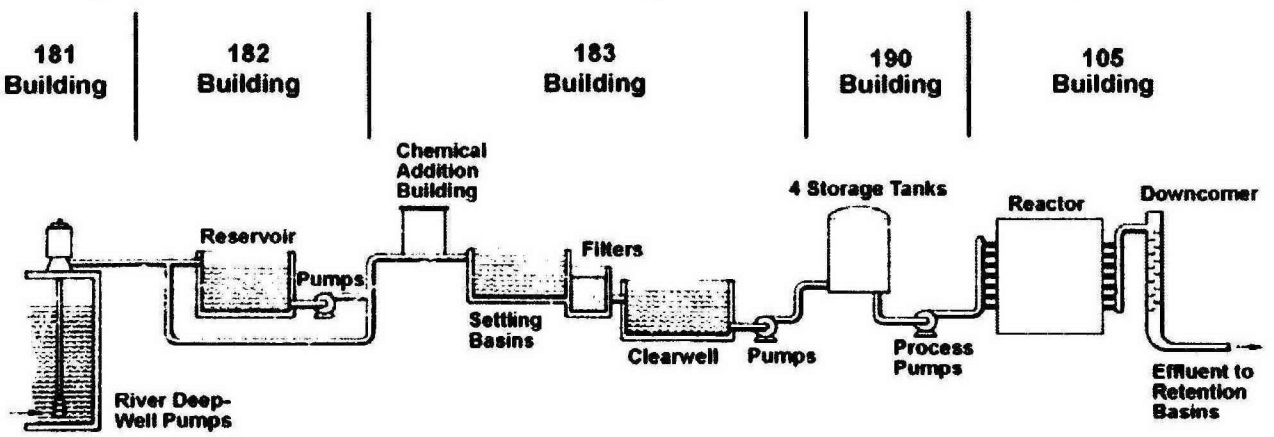
Groundwater flow velocities in the shallow unconfined aquifer in the 100-D Area have been evaluated in the vicinity of the ISRM treatment zone using various measurements of aquifer characteristics, including the performance of a natural gradient aquifer tracer test (*100-D Area In Situ Redox Treatability Test for Chromate-Contaminated Groundwater* [PNNL-13349]). The results of these tests indicated that groundwater velocity varied widely as a function of the local aquifer lithology, ranging from about 0.3 to 2 m/day (1 to 7 ft/day). Although this investigation was focused on a relatively small portion of the aquifer, the highly variable flow velocities that were encountered likely reflect the heterogeneous nature of the Hanford formation and Ringold Unit E present in the 100-D Area as a whole.

2.4 HISTORICAL SITE OPERATIONS AND POTENTIAL SOURCES OF CONTAMINATION

As previously discussed, the 100-D Area is the site of two retired plutonium-production reactors, the D and DR Reactors. The D Reactor operated from 1944 to 1967, and the DR Reactor operated from 1950 to 1965. The D and DR Reactors were designed to use the once-through cooling process, in which cooling water pumped from adjacent Columbia River was processed to remove solids and was treated for corrosion resistance before passing through the reactor to cool the core. Sodium dichromate salts and aqueous solutions of varying concentrations were routinely added to the cooling water stream in order to reduce the corrosivity of the water. After passing through the reactor, the spent cooling water (typically containing approximately 2 mg/L of hexavalent chromium) were discharged to unlined basins, where it was held for a number of hours to allow decay of short-lived activation products before being piped back to the Columbia River. A schematic diagram of the reactor cooling system is shown in Figure 2-7. The discharge of cooling water to unlined basins at the 100-D Area led to widespread mounding of the aquifer, with spent cooling water containing about 2 mg/L of hexavalent chromium. Upon cessation of reactor operations in 1967, the cooling-water component of the contaminated groundwater has largely dispersed.

Nevertheless, an extensive hexavalent chromium plume remains at the site with concentrations that are locally much higher than 2 mg/L. This suggests that there have been leaks or spills of more concentrated hexavalent chromium solutions that are continuing to contaminate 100-D Area groundwater. The higher concentration materials that were used at the site include sodium dichromate salt and high- to moderate-concentration sodium dichromate solutions (e.g., 10% working solutions, or 70% stock solutions). These concentrated materials were used as the feed and working stock solutions for the production of the 2 mg/L dichromate-amended cooling water. These concentrated materials were used at the locations and facilities shown in Figure 2-8 and listed below:

Figure 2-7. Generalized Schematic Flow Diagram of Hanford Reactor Cooling Water.



SOURCE: *History of the Plutonium Production Facilities at the Hanford Site Historic District, 1943-1990* (DOE/RL-97-1047).

Figure 2-8. Location of 100-D Facilities Historically Associated with the Use of Concentrated Hexavalent Chromium Salts and Solutions.

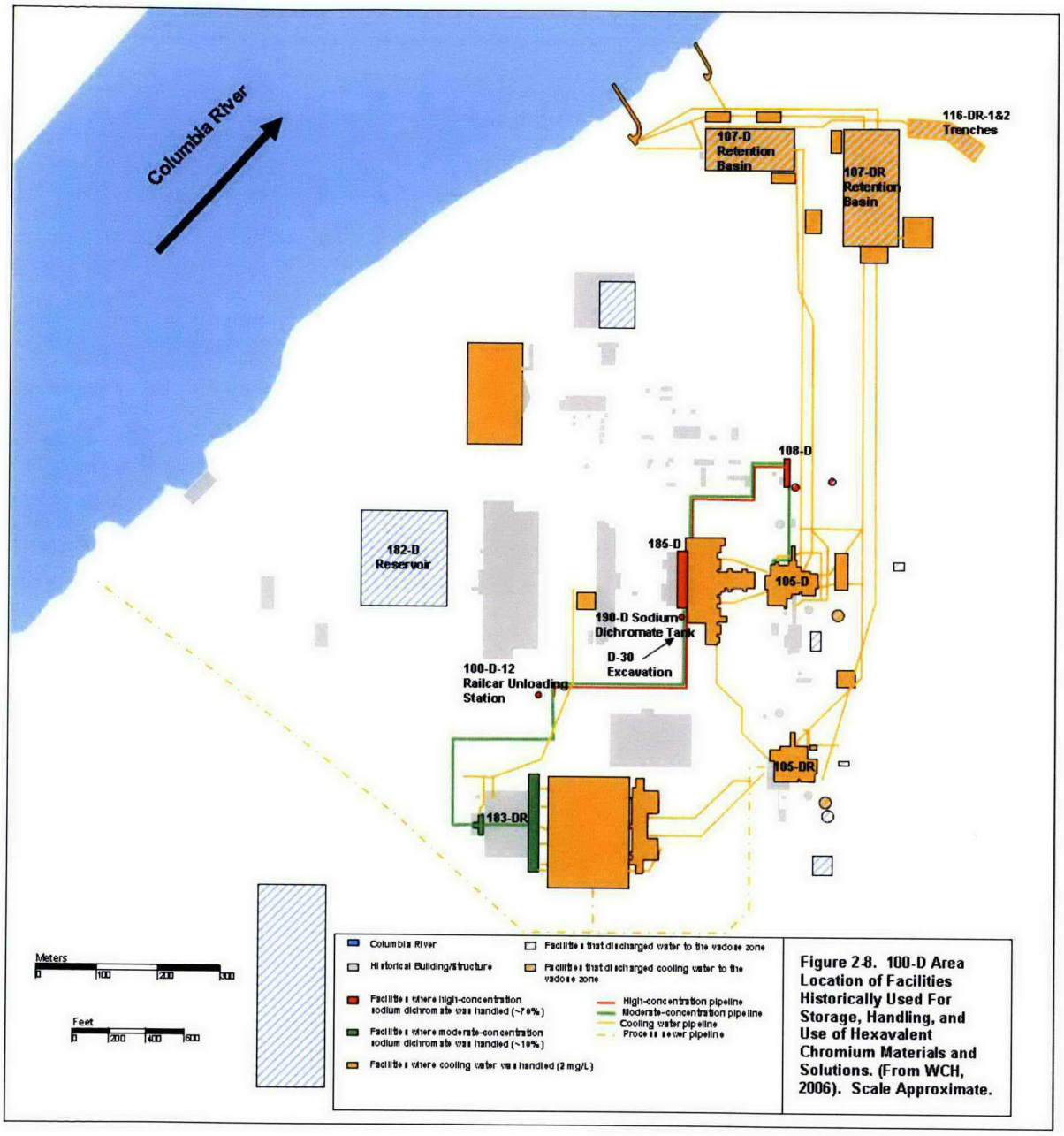


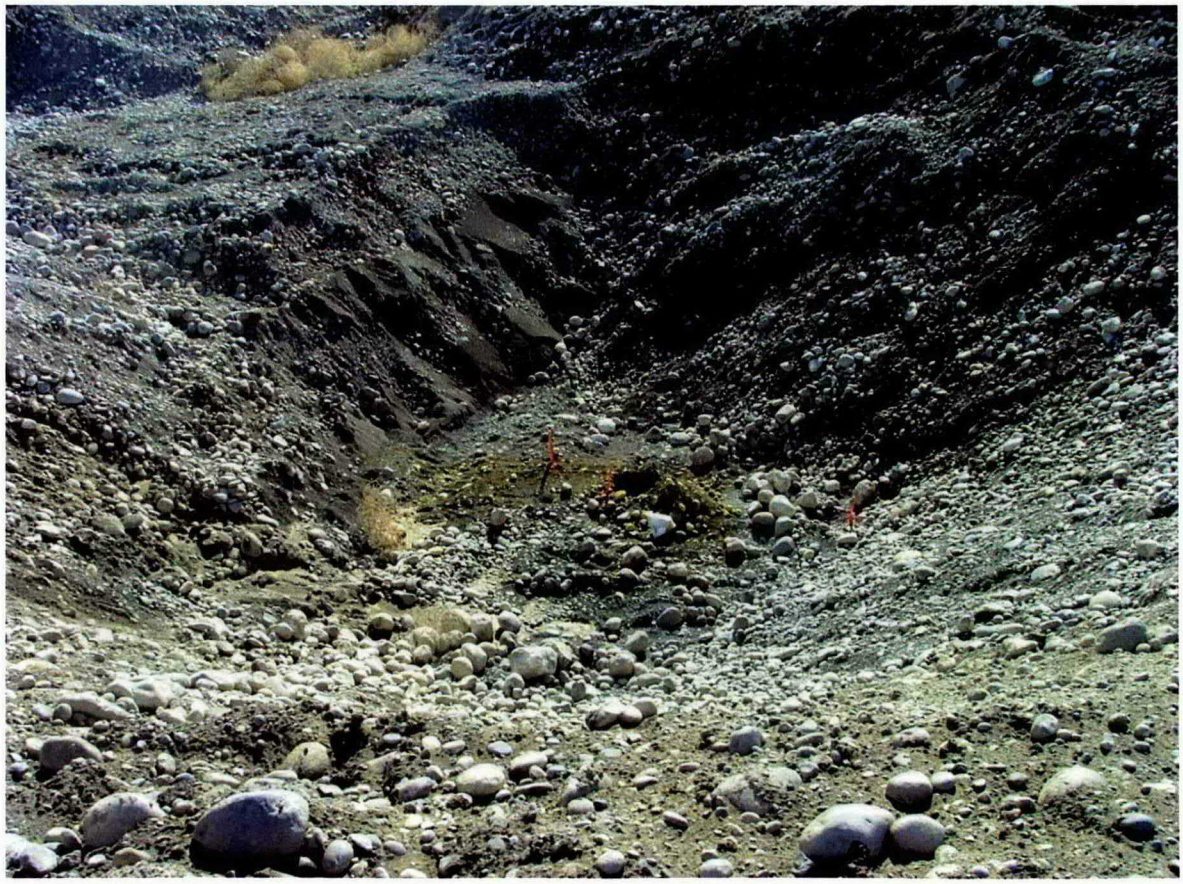
Figure 2-8. 100-D Area Location of Facilities Historically Used For Storage, Handling, and Use of Hexavalent Chromium Materials and Solutions. (From WCH, 2006). Scale Approximate.

- 108-D Building and its associated waste disposal cribs (storage and handling of sodium dichromate salt and high- and moderate-concentration solutions; disposal to ground of chromium-bearing decontamination solutions)
- 185-D and 190-D Buildings and the solution storage tank location adjacent to former 190-D Building (storage and handling of high- and moderate-concentration solutions)
- Former railcar unloading station (handling of high-concentration solutions)
- 183-DR Building (handling of moderate-concentration solutions).

Several investigations have been conducted at the 100-D Area to investigate (largely unsuccessfully) for residual secondary sources of hexavalent chromium contamination in surface soils and the deeper vadose zone around these facilities. For example, extensive sampling and analysis of sediments in the vicinity of the former 183-DR Building (Figure 2-8) did not reveal the presence of substantial subsurface soil contamination. Additional sampling and analysis were conducted near the 190-D Building and a former transfer pipeline where chromium-stained surface soils had been observed. A recent 2008 excavation into the vadose zone near the southwest corner of the 190-D Building (see approximate location of D-30 in Figure 2-8) revealed visible hexavalent chromium contamination in the vadose zone at a depth of 5.5 to 6.1 m (18 to 20 ft) bgs in sandy, pebbly, and cobbly materials of the Hanford formation (Figure 2-9).

Despite the limited success in finding substantial vadose zone contamination associated with most of the abandoned infrastructure systems (e.g., tanks and pipelines) that are suspected to be potential source areas, these sites should be considered for re-evaluation if groundwater quality data from new or existing monitoring wells suggests that a continuing source of groundwater contamination is present in their vicinity. Alternatively, an in situ remedial approach that does not require the precise identification of vadose zone sources in a target area should be considered.

Figure 2-9. Excavation D-30 Located Near the Southwest Corner of the 190-D Building Showing Discoloration from Hexavalent Chromium at a Depth of About 5.5 to 6.1 m (18 to 20 ft) Below Ground Surface.



2.5 NATURE AND EXTENT OF HEXAVALENT CHROMIUM CONTAMINATION

With the exception of areas affected by the sodium dithionite-based ISRM, the general chemistry of the shallow unconfined aquifer at the 100-D Area groundwater can be described as moderately alkaline with dissolved oxygen concentrations that are at or near equilibrium with air. The major cationic species are dominated by sodium, calcium, and magnesium, and the non-carbonate anionic species are dominated by sulfate and nitrate. The pH of the groundwater is slightly basic, typically between 7.5 and 8, and the groundwater approaches saturation with respect to calcium carbonate.

Hexavalent chromium is widely distributed within the shallow unconfined aquifer at the 100-D Area. There remains considerable uncertainty, however, regarding the magnitude and distribution of hexavalent chromium contamination within the Ringold Upper Mud. Most of the monitoring wells at 100-D Area are completed within the unconfined aquifer above the Ringold Upper Mud and, as a result, do not monitor conditions within the Ringold Upper Mud. Monitoring the water-bearing unit(s) within the Ringold Upper Mud is complicated by the potential presence of relatively thin and possibly discontinuous sand units within the fine-textured Ringold Upper Mud and the uncertainty in defining the hydraulic pathways by which contaminated water from the overlying unconfined aquifer may move into, and out of, those hydraulically active units within the Ringold Upper Mud. Currently, only one monitoring well (199-D8-54A) is screened within the Ringold Upper Mud, and it has relatively low concentrations of hexavalent chromium (generally <30 μg/L). However, it is anticipated that hexavalent chromium concentrations in the shallow unconfined aquifer are much higher and far more widespread. The extent of hexavalent chromium contamination in the Ringold Upper Mud will be evaluated as part of the upcoming RI.

As previously discussed, constituents of interest present in the 100-D Area groundwater include strontium-90, tritium, nitrate, and sulfate. The nitrate, sulfate, tritium, and strontium-90 in the 100-D Area groundwater did not necessarily originate from the same primary sources as the hexavalent chromium, however, they are in some instances currently co-located with the hexavalent chromium plumes. The maximum observed 2006 concentrations of hexavalent chromium and the other constituents are compared in Table 2-1.

The persistence of elevated concentrations of hexavalent chromium in the 100-D Area groundwater more than 40 years after the reactors were shut down, and after several years of pump-and-treat remediation, indicates that the current distribution of hexavalent chromium in the groundwater at the 100-D Area is not just a remnant of the historical reactor coolant recharge. Rather, it is probable that the groundwater continues to be contaminated by the periodic or steady release of hexavalent chromium from localized zones of chromate contamination within the overlying vadose zone. These areas of vadose zone contamination were likely produced by numerous inadvertent releases or leaks of sodium dichromate salt or moderately to highly concentrated sodium dichromate solutions from pipes, storage areas, and other process facilities, to the ground surface or shallow subsurface.

Table 2-1. Concentrations of Chromium and Other Selected Groundwater Constituents at the Hanford Site 100-D Area.

Constituent	Maximum Concentration Reported Fall 2007	Co-Located with Chromium?
Hexavalent chromium (Cr^{+6})	10,900 µg/L	Not applicable
Nitrate (NO_3^-)	86 mg/L	Yes
Strontium-90 (Sr-90)	<9 pCi/L	No
Tritium (H-3)	~12,000 pCi/L	No
Sulfate (SO_4^{-2})	140 mg/L	Yes

SOURCE: As reported in *Hanford Site Groundwater Monitoring for Fiscal Year 2007* (DOE/RL-2008-01).

NOTE: The principal contaminant of concern in the 100-D Area is hexavalent chromium. Strontium-90, tritium, and nitrate are constituents of interest that are actively monitored but are present in concentrations that result in low ecological risk (*Limited Field Investigation Report for 100-HR-3* [DOE/RL-93-43]). Sulfate is of interest because the secondary drinking water standard has been exceeded in the past in a limited number of wells.

The chromium contamination at the 100-D Area consists of separate northern and southern plumes (Figure 2-10). This separation of the 100-D Area groundwater contamination into discrete northern and southern plumes has been attributed, in large part, to chronic leakage of raw water from the 182-D reservoir, resulting in the formation of a discernable groundwater mound within the overall contaminant footprint of the 100-D Area. Recent changes in operating practices at the reservoir (e.g., reducing the operating water level) have reduced the magnitude of the leakage and the underlying mound. Consequently, the extent of groundwater flow diversion and plume dilution beneath the reservoir has been reduced. Consequently, the southern and northern plumes may soon merge, producing a single, large, contiguous plume.

Currently, both plumes are discharging to the Columbia River and potentially impacting the river's ecosystem. Hexavalent chromium-contaminated groundwater is locally upwelling into river gravels potentially used for salmon spawning (redds) and, during low-river stages, seeps from shoreline springs are discharging to riparian habitat.

2.5.1 Southern Plume

The southern plume appears to originate in the vicinity of the railcar transfer station and generally migrates to the west, toward the ISRM treatment zone. Past depictions of the leading edge of the southern plume have suggested that relatively little hexavalent chromium has been able to migrate past the ISRM treatment zone and discharge to the river. More recent interpretation incorporates hexavalent chromium data for wells within the ISRM treatment zone, indicating that a northern section of the ISRM barrier is not treating all of the plume reaching the barrier in this area. That portion of the plume not intercepted by the ISRM treatment zone is expected to eventually discharge to the river.

Although the southern plume has historically had the highest hexavalent chromium concentrations in the 100-D Area, recent characterization activities have substantially increased

the known extent and concentrations of hexavalent chromium in the upgradient part of this plume. In 2007, seven boreholes (Figure 2-10) were advanced and monitoring wells were installed in the upgradient portion of the southern plume as part of a source area investigation. Two of these borings (199-D5-104 and 199-D5-99) were advanced in the vicinity of the former railcar unloading station where bulk sodium dichromate solutions were historically handled. These two locations yielded groundwater with hexavalent chromium concentrations of more than 5,000 μg/L in 2007, substantially higher than any concentrations previously observed in the 100-D Area. A groundwater sample collected from 199-D5-99 in March 2008 yielded distinctly yellowish groundwater, with hexavalent chromium concentrations approaching 40,000 μg/L. These new observations strongly support the existence of a source of hexavalent chromium in the vicinity of these wells (potentially in the vadose zone around the transfer station). It is not known, however, whether these elevated concentrations in the groundwater represent a relatively recent development or if they simply reflect better characterization of the plume near an ongoing, long-term release of contamination from the overlying vadose zone. A diagram illustrating a conceptual model for the possible origin of the southern plume in general, and the hot spot area in particular, is presented in Figure 2-11.

2.5.2 Northern Plume

The northern plume is larger and more diffuse than the southern plume, and it appears to be generally migrating from the vicinity of the 105-D Building (the D Reactor) to the north and northwest (Figure 2-8). It has substantially lower maximum concentrations of hexavalent chromium than the southern plume and is typified by concentrations of hexavalent chromium between 100 and 1,000 μg/L. The maximum concentration of hexavalent chromium observed in this plume over the last few years was approximately 2,500 μg/L in May 2007 in monitoring well 199-D5-15. The concentrations in this well declined to 852 μg/L by November 2007 (*Calendar Year 2007 Annual Summary Report for the 100-HR-3, 100-KR-4, and 100-NR-2 Operable Unit Pump-and-Treat Operations* [DOE/RL-2008-05]).

The long-term persistence of the hexavalent chromium concentrations in the northern plume suggests that it is also being fed by continuing (perhaps vadose zone) sources. Relatively few borings and monitoring wells are located in the upgradient portion of the northern plume, and there is limited information available to identify and characterize the apparent secondary source(s) in that area. The available data suggest that the source areas for the northern plume are distinct from, and perhaps more widely dispersed than, the source area(s) for the southern plume. Additional field characterization will be conducted under the 100 Areas RI.

Figure 2-10. Distribution of the 100-D Area Hexavalent Chromium Plumes in Spring and Fall 2007.

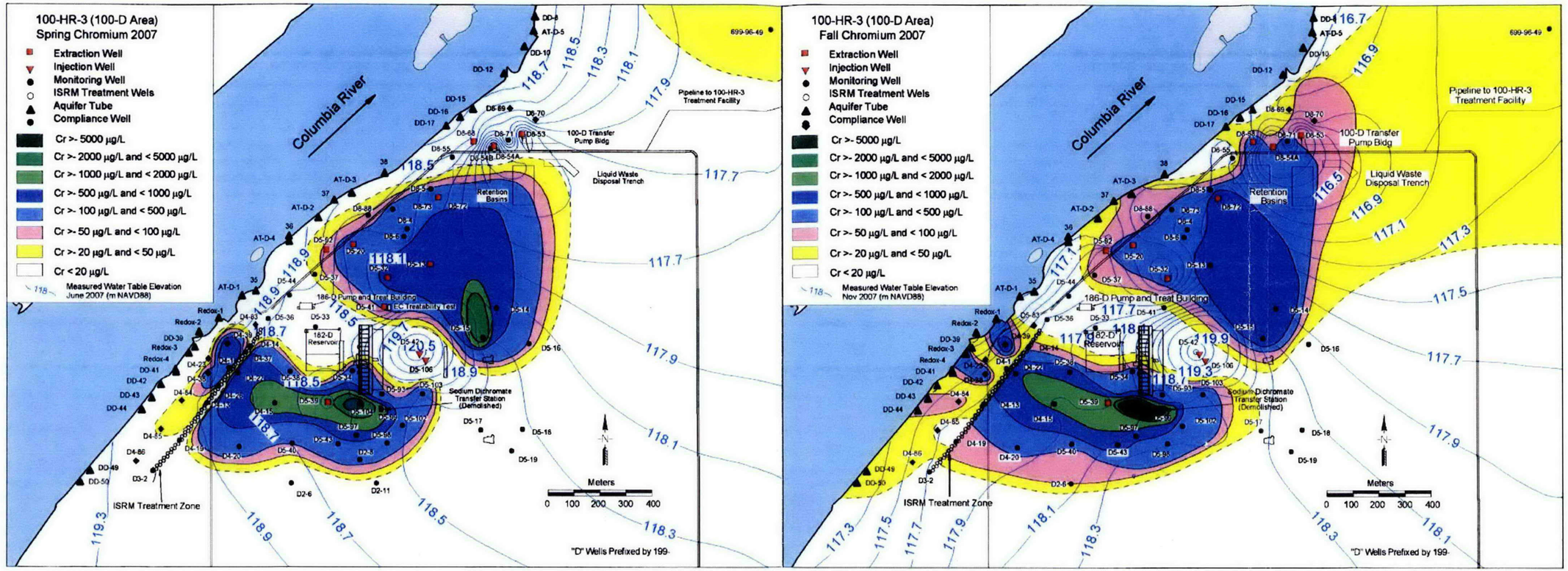
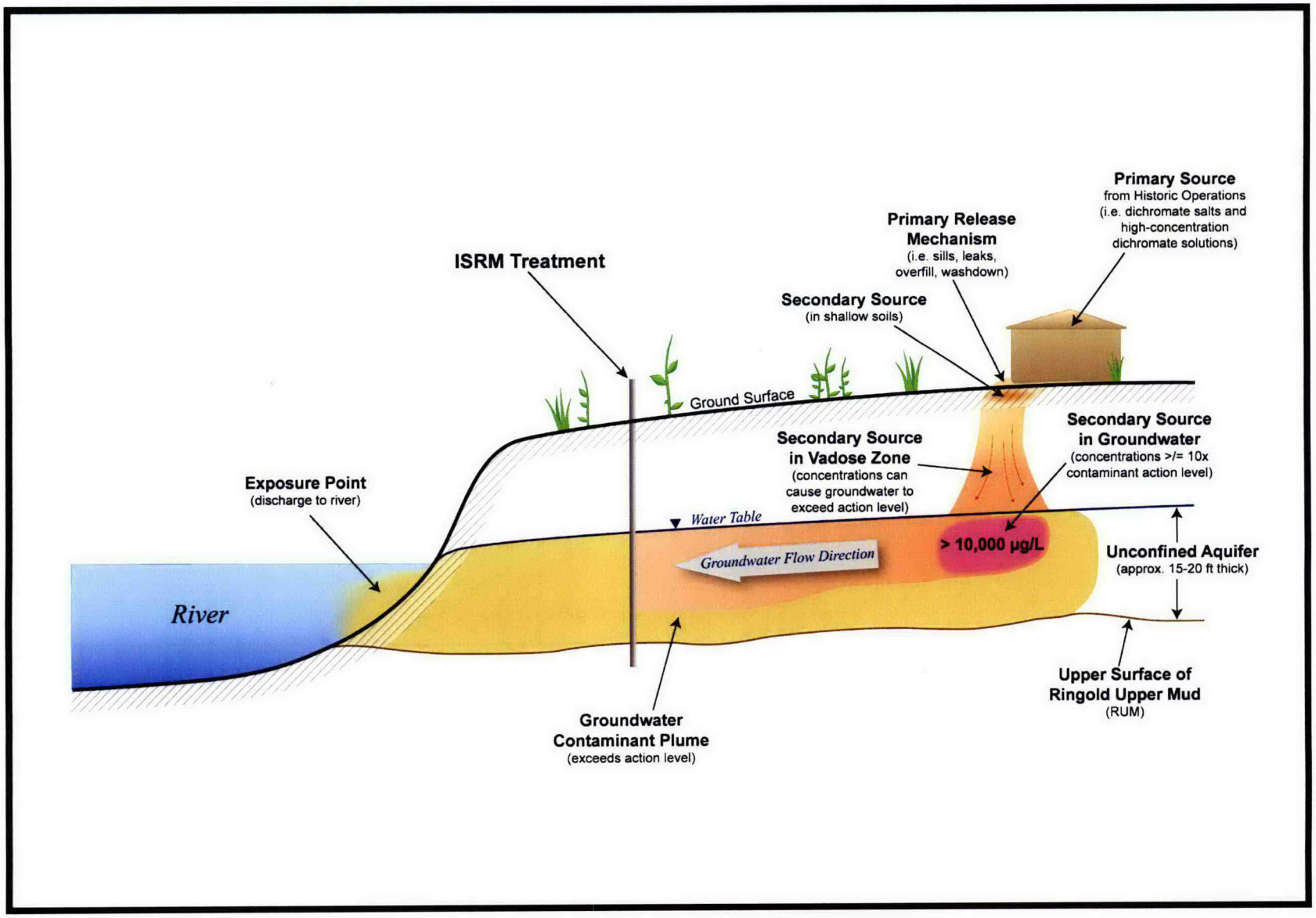


Figure 2-11. Conceptual Model of Southern Plume and Potential Vadose Zone Contamination in the Vicinity of the Railcar Transfer Station Hot Spot.



2.6 IMPLICATIONS FOR CURRENT AND POTENTIAL FUTURE REMEDIAL ACTIONS

Despite the remedial actions that have been active at the site for several years and the relatively rapid rate of groundwater flow through the shallow unconfined aquifer, the extent and concentrations of hexavalent chromium contamination at the site have not notably diminished. This persistence of elevated concentrations of hexavalent chromium in groundwater at the 100-D Area suggests the presence of continuing sources. Although the potential for continuing releases from existing infrastructure should be investigated, there is substantial evidence that at least some of the groundwater contamination is being fed by long-term secondary sources in the vadose zone. Consequently, successful long-term remediation of groundwater contamination at the 100-D Area will not only require the continued elimination of any remaining primary sources (e.g. leaking pipelines), but the continued remediation of secondary sources of hexavalent chromium in the vadose zone will also be necessary. It is probable that hexavalent chromium exceedances would exist in the aquifer for decades unless the secondary sources in the vadose zone are identified and remediated. Decommissioning of reactor area structures and cleanup of associated shallow vadose soil (e.g., generally to a depth of about 5 m [16 ft] bgs) has been completed at most locations within 100-D Area by contractors working under the River Corridor Contract and its predecessor, the Environmental Restoration Contract. The River Corridor Contract contractor is continuing with characterization and remediation activities at the 100-D Area.

The interim remedial actions implemented at the 100-D Area (i.e. the ISRM treatment zone at the southern plume, and the DR-5 and the 100-HR-3 pump-and-treat systems to the north) were primarily designed to protect the river by intercepting downgradient portions of the plumes and reducing or eliminating the discharge of hexavalent chromium to the river at concentrations >20 μg/L. Although the existing systems have reduced the levels of hexavalent chromium discharging to the river, they have not been able to eliminate hexavalent chromium exceedances at the river, nor have they been able to substantially reduce the concentrations and extent of hexavalent chromium contamination in the upgradient areas of the plumes. These systems were never intended to address, nor are they capable of addressing, secondary sources in the vadose zone or to remediate the existing upgradient hot spots in a timely fashion. Unless additional actions are taken to accelerate the cleanup of the residual source areas and plume hot spots, it will likely be necessary to operate the existing systems for decades.

2.7 CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations emerged during the review of the CSM, as it is currently understood:

- The current remedial actions do not appear to sufficiently address the hexavalent chromium contamination in the groundwater of the 100-D Area and are not preventing groundwater with hexavalent chromium exceedances from discharging to the Columbia River.
- One potential reason for the failure of the current remedial actions is that they do not sufficiently address continuing sources of hexavalent chromium that are present in the vadose zone.

- Identification and excavation of localized secondary sources of hexavalent chromium in the deep vadose zone may be problematic. In situ treatment should be considered as a remedial option for areas (if any) where one or more unidentified sources of deep vadose zone contamination are suspected to be present.
- The southern plume hot spot is likely in the immediate vicinity of a substantial vadose zone source of hexavalent chromium.
- The vadose zone source area(s) for the northern plume are not sufficiently characterized. The northern plume may be sourced by numerous localized zones within the footprint of the plume. Identification and excavation of numerous small spills in the vadose zone of the 100-D Area plume will be problematic.
- Installation of additional monitoring wells could be considered in the suspected source areas of the northern plume in order to determine if elevated levels of hexavalent chromium in the groundwater can be used to confirm the general location(s) of vadose zone sources.
- More detailed vadose zone soil characterization has been/should be incorporated into all future well drilling activities.

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3.0 REVIEW OF CURRENT EX SITU TREATMENT SYSTEMS AND OPTIMIZATION STUDIES

Consistent with the tasks identified for the 100-D Area RPO effort, this section presents a system and performance evaluation for the aboveground components of the ex situ treatment systems that have been deployed (100-HR-3 and DR-5) or tested (electrocoagulation) at the 100-D Area. Based on the evaluation of these three systems, potential actions and recommendations have been identified to optimize the existing aboveground treatment systems. This section does not address optimization of extraction well performance or optimization of capture zone development for these systems, as these factors will be addressed later in the RPO process.

The primary objectives of this section are as follows:

- Review and evaluate system performance data for the 100-HR-3 and DR-5 treatment systems
- Identify operational or design problems or limitations with these systems
- Make recommendations to improve system design and performance of these systems
- Determine whether electrocoagulation would be an effective and appropriate alternative to the current IX technologies.

Interim remedial actions for the 100-D Area were initiated in 1997 when the 100-HR-3 pump-and-treat system was installed to reduce the levels of hexavalent chromium in groundwater discharging to the Columbia River. Between 2000 and 2003, the 100-HR-3 system was augmented by the phased installation of the ISRM treatment zone (Figure 2-2). Although a review of the ISRM barrier is beyond the scope of this discussion, this system will likely remain an important part of the overall 100-D Area treatment system. An excellent summary of the history, current status, and proposed optimization efforts for the ISRM is presented in the *In Situ Redox Manipulation (ISRM) Annual Report Fiscal Year 2007* (DOE/RL-2008-10). Active treatment of the 100-D Area was further expanded in 2004 with the addition of a second IX pump-and-treat system, the DR-5 system. The DR-5 system was designed to capture hexavalent chromium contamination that is located in the southern portion of the northern plume.

Despite the installation and operation of these treatments systems, elevated concentrations of hexavalent chromium have persisted in the groundwater at the 100-D Area with little evidence of a substantial reduction in the plume extent or in hexavalent chromium concentrations. Nevertheless, ex situ treatment of contaminated groundwater will likely remain an important component of any future remedial actions for the 100-D Area.

In 2007, a pilot-scale treatability test of electrocoagulation ex situ treatment of hexavalent chromium in groundwater was conducted at the 100-D Area. The primary objectives of the treatability study were (1) to evaluate the effectiveness of hexavalent chromium removal and implementability of the system, and (2) to determine whether electrocoagulation is a potentially more robust and cost-effective alternative to the current IX technologies employed at the site.

3.1 100-HR-3 SYSTEM

The 100-HR-3 IX system was designed to remove hexavalent chromium from groundwater plumes in the 100-D and 100-H Areas (Figure 2-1). The system was installed in the 100-H Area, and a pipeline was constructed to transport water from the 100-D Area. Currently, groundwater from the 100-D and 100-H Areas is combined prior to treatment. Groundwater is collected from extraction wells at the northern plume in the 100-D Area and from the 100-H Area. The 100-HR-3 treatment system is housed in the 1713-H Building. A schematic flow diagram of the system is shown in Figure 3-1.

3.1.1 Design Goals/Criteria

Original design criteria for the 100-HR-3 system include the following (*Design Criteria and Design Basis for the 100-HR-3 and 100-KR-4 Pump and Treat System* [BHI-00772]):

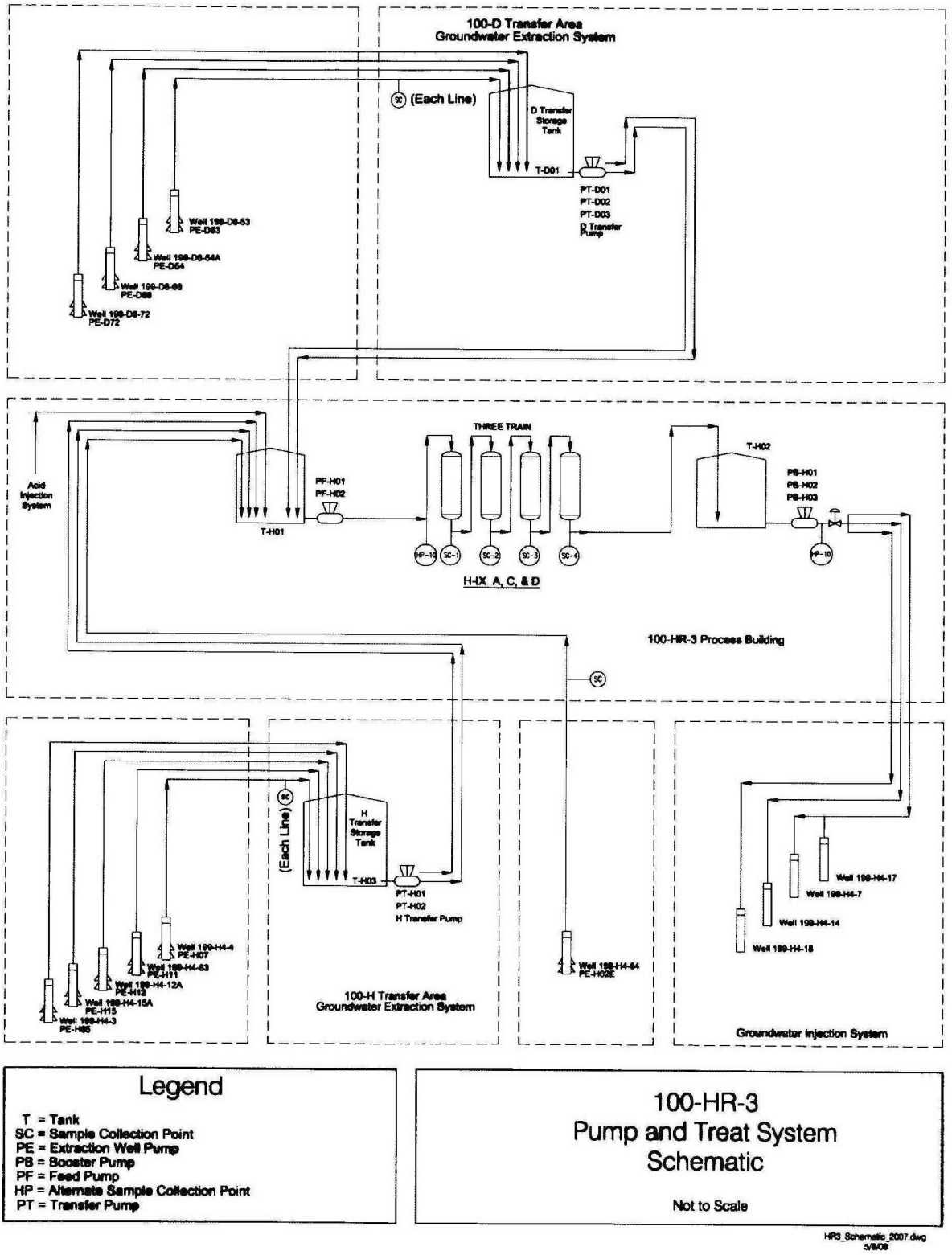
- Treat groundwater at a maximum flow of 1,500 L/min (400 gallons per minute [gpm]) with flow-weighted average influent hexavalent chromium concentrations of 225 µg/L.
- Reduce effluent hexavalent chromium concentrations to the maximum extent practicable. Treated groundwater with hexavalent chromium concentrations >50 µg/L will not be discharged.
- Operate on an essentially continuous basis with minimal impact from resin changes or routine maintenance.
- Operate unattended and uninterrupted with 90% total system availability.
- Use a modular design to allow increase or decrease in treatment capacity as required.

3.1.2 Current System Configuration

The 100-HR-3 treatment system uses resin that is regenerated offsite. The system design, resin type, and regeneration procedure at the 100-HR-3 system are similar to all of the other ion chromatography systems in the 100 Areas (with the exception of the DR-5 system).

The 100-HR-3 system consists of three skid-mounted treatment trains through which groundwater flows in parallel. Although the initial design flow rate capacity was 1,500 L/min (400 gpm), one of the original four IX trains was relocated to another Hanford groundwater treatment facility, reducing the current 100-HR-3 capacity to 1,135 L/min (300 gpm). However, the actual flow rates are limited by the current extraction rates and are generally <750 L/min (200 gpm). Any future requirement for increased flow capacity could be addressed by the installation of additional trains of the same design or, alternatively, by changing the existing system design.

Figure 3-1. 100-HR-3 Ion-Exchange System.



SOURCE: *Calendar Year 2006 Annual Summary Report for the 100-HR-3, 100-KR-4, and 100-NR-2 Operable Unit Pump-and-Treat Operations* (DOE/RL-2007-76).

3.1.2.1 100-D Area Extraction System. Water is collected from four extraction wells (199-D8-53, 199-D8-54A, 199-D8-68, and 199-D8-72) using submersible pumps. These wells, which are located in the north end of the 100-D Area, intercept the hexavalent chromium plume as it flows towards the northeast and eventually discharges to the river. Water is pumped from these wells to a 100-D Area transfer tank located at the 100-D transfer building, from which water is pumped overland to the 100-HR-3 processing facility, a distance of approximately 4.0 km (2.5 mi).

3.1.2.2 100-H Area Extraction System. Water is currently collected from six extraction wells (199-H4-3, 199-H4-4, 199-H4-12A, 199-H4-15A, 199-H4-63, and 199-H4-64) using submersible pumps. These wells are located approximately in a line adjacent to the river. The first three wells intercept groundwater from the area of the former 183-H solar collection basin. Groundwater from well 199-H4-64 is pumped directly to the processing facility. Groundwater from the remaining wells is pumped to the 100-H transfer building and from there to the processing facility, a distance of approximately 0.8 km (0.5 mi).

3.1.2.3 Influent Storage Tank and Water Transfer. Extracted groundwater is collected in an 11,350-L (3,000-gal) high-density polyethylene (HDPE) tank located inside the processing facility (1713-H Building). A sulfuric acid injection system reduces groundwater pH from 7.6 to 7.0 to prevent precipitation of calcium carbonate on piping and IX columns. The pH of the influent tank is manually adjusted based on the pH values monitored in the effluent tank (see below). Two process feed pumps transfer water to the IX column trains.

3.1.2.4 Ion-Exchange Trains. The IX columns are located in three skid-mounted trains with four columns in series per train. The column diameter is 1.36 m (4.46 ft) and the cross-sectional area is 1.45 m^2 (15.6 ft^2). Each column contains a resin volume of 2.27 m^3 (80 ft^3) and includes freeboard and space for bed volume expansion during backwash. The four columns in each train are valved to allow operation in any sequence. The maximum rated flow rate of each train is 379 L/min (100 gpm), and the maximum allowable pressure drop is 7.0 kg/cm^2 differential (kg/cm^2-d) (100 $lb/in.^2$ differential [psid]).

3.1.2.5 Resin. The resin is Dowex® 21K, 16-20 mesh, a Type 1 strong-base, anion-exchange resin in the chloride form (Dow 2008). It has a capacity of 1.2 equivalents/L and can operate at elevated temperatures and over a wide pH range. It is regenerated at a Siemens facility in Roseville, Minnesota.

3.1.2.6 Effluent Storage Tank. Treated effluent is collected in a 11,350-L (3,000-gal) HDPE tank located inside the processing facility (1713-H Building).

3.1.2.7 Backwash System. Prior to removal of resin for regeneration, the lead column is backwashed with water to remove fines from the resin. Water is cycled through the column during each cycle.

3.1.2.8 Reinjection. Treated water is injected into wells 199-H4-7, 199-H4-14, 199-H4-17, and 199-H4-18. These wells are upgradient of the 100-H Area extraction wells.

Dowex® is a registered trademark of the Dow Chemical Company, Midland, Michigan.

3.1.2.9 Monitoring. The IX system is monitored for influent flow rates, effluent pH, system pressures, and hexavalent chromium concentrations (influent, effluent, and between columns). Radioactivity levels are measured on spent resins prior to their shipment for regeneration.

3.1.3 Historical System Modifications

The current 100-HR-3 system reflects several modifications that were implemented in the past:

- Originally, four treatment trains were used at 100-HR-3. However, because extraction well production was lower than expected, one of the trains was moved to the 100-K Area.
- After initial operations, the system was configured to treat streams from the 100-D Area separately from the 100-H Area because technetium-99 was found in the 100-H Area wells. In 2005, the waste streams were combined to increase process efficiency (*100-HR-3 Pump and Treat Design Description* [CP-15943]).
- In 2004, the first column was converted to a sacrificial column, with resins disposed at the Environmental Restoration Disposal Facility (ERDF) because of the build-up of uranium in the resin (*Calendar Year 2004 Annual Summary Report for the 100-HR-3, 100-KR-4, and 100-NR-2 Operable Unit Pump-and-Treat Operations* [DOE/RL-2005-18]). Resin from the second column was regenerated offsite. After the *Authorized Limit Application for the Regeneration of Ion Exchange Resin at 100-HR-3 and 100-KR-4 Operable Units* (FH-0700035A) was approved in 2007 allowing offsite shipment of resins contaminated with radionuclides, spent resins from the first column were also shipped offsite for regeneration.
- Configurations of 100-H Area wells were modified during 2005 and 2006. At the beginning of calendar year 2005 (CY05), extraction wells included 199-H3-2A, 199-H4-7, 199-H4-11, 199-H4-12A, 199-H4-15A, and 199-H4-65. The current configuration includes wells 199-H4-3, 199-H4-4, 199-H4-12A, 199-H4-15A, 199-H4-63, and 199-H4-64. The previous injection wells included 199-H3-3, 199-H3-4, and 199-H3-5. The current configuration includes wells 199-H4-7, 199-H4-14, 199-H4-17, and 199-H4-18 (*Calendar Year 2005 Annual Summary Report for the 100-HR-3, 100-KR-4, and 100-NR-2 Operable Unit Pump-and-Treat Operations* [DOE/RL-2006-08]; *Calendar Year 2006 Annual Summary Report for the 100-HR_3, 100-KR-4, and 100-NR-2 Operable Unit Pump-and-Treat Operations* [DOE/RL-2007-76]).

3.1.4 System Operation and Process Description

In the IX process, groundwater is pumped through columns containing an anion-exchange resin that removes hexavalent chromium. Water flow in the IX system is from top to bottom in each column and sequentially through four columns (i.e., lead, lag 1, lag 2, and polish). After spent resin in the lead column is removed for regeneration (with an eductor system) and replaced, this column becomes the polishing column, and the remaining columns move up in sequence. Flow can continue through three columns while resin in the lead column is being changed out. Resins are removed for regeneration when the hexavalent chromium concentration leaving the polishing column exceeds 5 μg/L.

After backwashing to remove fines, the resin in the lead column is fed by flow of treated water into two totes, each having a volume of approximately 1.1 m^3 (40 ft^3). The totes are placed in a containment area to allow the water to drain. After the totes have been drained of excess water and the resin sampled for radioactivity, the totes are shipped offsite. Regenerated resins are returned in the same totes. Based on the volume of regenerated resin in the totes, fresh resin is added to make up for any losses.

The process used at the Siemens facility for regeneration of Dowex 21K resin is as follows (FH-0700035A):

- Up-flow each tote with 1.1 m^3 (40 ft^3) with soft water at 114 L/min (30 gpm) to remove solids
- Down-flow with 1.1 m^3 (40 ft^3) of 4% sodium hydroxide/10% sodium chloride solution at 95 L/min (25 gpm) to remove hexavalent chromium
- Down-flow with 3.4 to 4.5 m^3 (120 to 160 ft^3) of 8% sodium chloride solution at 95 L/min (25 gpm) to convert the resin to the chloride form
- Slow rinse with 1.1 m^3 (40 ft^3) soft water at 95 L/min (25 gpm)
- Fast rinse with 2.3 m^3 (80 ft^3) soft water at 189 L/min (50 gpm).

Backwash and rinse water, except for the final fast rinse, are transferred to a holding tank where the pH is reduced to 2.5 to 3.0 with sulfuric acid. Sodium metabisulfite is added to reduce hexavalent chromium to trivalent chromium, and lime is added to raise the pH to 9.5 to 10.0 to precipitate out trivalent chromium hydroxides. Residual liquid waste is conveyed to a municipal wastewater treatment facility, along with the final fast rinse water, and the recovered solids are sold for production of high-strength concrete.

During CY05 and CY06, the only significant solid waste generated from the 100-HR-3 system was 195 m^3 (6,900 ft^3) of resin from sacrificial columns that was disposed of at the ERDF (DOE/RL-2006-08, DOE/RL-2007-76).

Anionic constituents present in the 100-D and 100-H Areas with the potential to bind to resins include nitrate and sulfate. Radionuclides typically present in anionic form with the potential to bind to resins include uranium [as $UO_2(CO_3)_2^{-4}$] and technetium-99 (as TcO_4^-). These constituents are typically present at higher concentrations in the 100-H Area wells located downgradient of the former 183-H solar evaporation basin (wells 199-H4-3, 199-H4-4, and 100-H4-12). Extraction well flow rates and average concentrations of hexavalent chromium and other constituents measured during fall 2006 (DOE/RL-2007-76) are presented in Table 3-1. For purposes of comparison, flow-weighted average nitrate and sulfate concentrations in the four DR-5 extraction wells were 26 and 60 mg/L, respectively. Drinking water maximum contaminant levels (MCLs) for nitrate and sulfate are 45 and 250 mg/L, respectively. The MCLs for uranium and technetium-99 are 30 μg/L and 900 pCi/L, respectively. Uranium and technetium-99 are not contaminants of concern in the 100-D Area. Sulfate is not a contaminant of concern in the 100-H Area.

3.1.5 Operational Performance

The 100-HR-3 system has been in operation since 1997. The operational performance of the system from January 2004 through December 2007 is summarized in Table 3-2. Performance data were obtained from annual summary reports (DOE/RL-2005-18, DOE/RL-2006-08, DOE/RL-2007-76, DOE/RL-2008-05).

During the period CY04 through CY07, 1,353 million L (357 million gal) of groundwater were treated and 122 kg (269 lb) of hexavalent chromium were extracted. The average total availability of the system was 97.2%.

Table 3-1. Flow Rates and Concentrations of Hexavalent Chromium and Other Constituents in 100-HR-3 Extraction Wells.

Extraction Wells	Flow (gpm)	Hexavalent Chromium (µg/L)	Nitrate (mg/L)	Sulfate (mg/L)	Uranium (µg/L)	Tc-99 (pCi/L)
199-D8-53	18.1	95	30	N/A	N/A	N/A
199-D8-54A	33.7	94	25	N/A	N/A	N/A
199-D8-68	52.5	107	36	78	N/A	N/A
199-D8-72	17.4	534	50	83	N/A	N/A
100-D Area	**121.7[a]**	**162.7**	**34[b]**	**79[b]**	**N/A**	**N/A**
199-H4-3	6.6	14	43	N/A	12.8	57
199-H4-4	8.1	18	N/A	N/A	7.3	54
199-H4-12A	9.7	23	37	N/A	9.8	50
199-H4-15A	19.9	26	N/A	N/A	1	0
199-H4-63	24.6	16	N/A	N/A	1	0
199-H4-64	16.6	20	23	N/A	3	0
100-H Area	**85.5[a]**	**19.9**	**31[b]**	**N/A**	**4[b]**	**15[b]**
Overall	**207.2[a]**	**103.8**	**33[b]**	**N/A**	**2[b]**	**6[b]**

[a] Total flow.
[b] Flow-weighted average.
N/A = not applicable

Table 3-2. 100-HR-3 System Operational Performance (Calendar Years 2004 Through 2007). (2 sheets)

	CY04	CY05	CY06	CY07
100-D Area total flow, million L (million gal)	164.2 (43.38)	189.4 (50.04)	229.4 (60.61)	170.5 (45.05)
100-H Area total flow, million L (million gal)	153.5 (40.55)	136.2 (35.98)	164.6 (43.49)	144.9 (38.28)
Total time, hours	8,784	8,760	8,760	8,760
Planned downtime, hours	73	209	60	55
Unplanned downtime, hours	1	515	16	41
Total operating time, hours	8,710	8,036	8,684	8,664
Scheduled availability, percent[a]	99.99	94.1	99.8	99.5

Table 3-2. 100-HR-3 System Operational Performance (Calendar Years 2004 Through 2007). (2 sheets)

	CY04	CY05	CY06	CY07
Total availability, percent[b]	99.2	91.7	99.1	98.9
Flow rate, L/min (gpm)	608 (160.6)	675 (178.4)	756 (199.8)	607 (160.3)
Flow rate, bed volumes/hour	16.1	17.9	20.0	16.0
Velocity, m/min (ft/min)	0.41 (1.35)	0.15 (0.50)	0.17 (0.56)	0.14 (0.45)
Hexavalent chromium mass, kg (lb)	33.6 (74.1)	33.5 (73.9)	33.1 (73.0)	21.8 (48.1)
100-D-Area hexavalent chromium concentration, μg/L	194	220	128	119
100-H-Area hexavalent chromium concentration, μg/L	23.5	30.0	22.0	16.0
Overall influent hexavalent chromium concentration, μg/L	111.6	140.5	83.7	71.7
Removal efficiency, percent	95.2	93.5	93.6	95.7
Effluent hexavalent chromium concentration, μg/L[c]	5.4	9.1	5.4	3.1
Regeneration frequency, columns/year	36	30	32	21
Regenerated resin installed, m^3 (ft^3)	40.8 (1,441)	63.4 (2,239)	61.2 (2,161)	47.6 (1,681)
New resin installed, m^3 (ft^3)	40.8 (1,441)	4.5 (159)	11.3 (399)	0.0 (0.0)
Resin turnover, percent[d]	50.0	6.6	15.6	0.0
Hexavalent chromium mass/regeneration cycle, kg (lb)	0.93 (2.06)	1.12 (2.46)	1.03 (2.28)	1.04 (2.29)
Accumulation rate, g/L (lb/ft^3)	0.411 (0.026)	0.492 (0.031)	0.456 (0.028)	0.457 (0.029)
Hexavalent chromium equivalent weight, grams/equivalent	26.0	26.0	26.0	26.0
$Capacity_{actual}$, equivalents[e]/L	0.016	0.019	0.018	0.018
$Capacity_{theoretical}$, equivalents/L	1.20	1.20	1.20	1.20
Capacity fraction, percent[f]	1.32	1.58	1.46	1.47

[a] Scheduled availability = 100 x (total available time-unplanned downtime)/total available time.
[b] Total availability = 100 x (total available time-total downtime)/total available time.
[c] Effluent hexavalent chromium concentration = influent concentration x removal efficiency.
[d] Resin turnover = 100 x (volume of new resin installed/volume of total resin installed).
[e] Equivalents are units of negative charge carried by anions.
[f] Capacity fraction = 100 x (actual capacity/theoretical capacity).
CY = calendar year
gpm = gallons per minute

The average influent hexavalent chromium concentration during this period was 165 μg/L from the 100-D Area and 22.9 μg/L from the 100-H Area. The average removal efficiency was 94.5%, yielding an average effluent concentration of 5.8 μg/L. This represents 96% removal efficiency for groundwater from 100-D Area wells and 75% efficiency from 100-H Area wells.

The average mass of hexavalent chromium regenerated was 1.03 kg (2.3 lb) per regeneration cycle. The actual capacity of the resin based on the quantity removed prior to decrease in performance is 1.46% of the theoretical capacity. This suggests that there is significant competition by anionic species, especially those included in Table 3-1.

Since beginning operations in 1997, the 100-HR-3 system has treated 3,030 million L (800 million gal) of groundwater and removed 323 kg (710 lb) of hexavalent chromium. During the period from CY04 through CY07, system operation has easily exceeded the 90% goal for total availability. Effluent hexavalent chromium concentrations during this period were generally below 20 μg/L with only one sample (in 2004) having a hexavalent chromium concentration >50 μg/L (DOE/RL-2005-18).

The Dowex 21K resin has been regenerated an average of five times/column, to date, which is well within the estimated maximum of 30 times per column. During the period from CY05 through CY07, 15.9 m^3 (560 ft^3) of new resin were installed. The turnover rate (volume of new resin divided by volume of total resin) during that period was 7.4%.

3.1.6 Process Optimization Status

A pilot-scale test bed system is being set up by FH to evaluate several resins under various operating conditions and chemical adjustments to evaluate resin loading capacities. The system will include several columns that can be operated independently, in parallel, or in series. The first proposed optimization test will be an evaluation of SIR-700, which is a Type I, weak-base anion resin designed for removal of hexavalent chromium (*SIR-700 and SIR-1200 Ion-Exchange Resin Technical Information* [ResinTech 2008][1]) with a significantly higher (2.5 times greater) capacity when the feed pH is approximately 6.0 and lower unit cost than Dowex 21K resin. The U.S. Environmental Protection Agency (EPA) had promising results with this resin at the Boomsnub/Airco site in Vancouver, Washington. Spent resin would be disposed at the ERDF rather than being regenerated. The existing eductor system was designed to remove the spherical, strong-base resin beads that are currently in use. A new system would likely be required to efficiently remove the more irregularly shaped beads typical of the weak-base resins being tested, should the system be converted to this resin type.

An alternative resin being considered is SIR-1200, claimed by the manufacturer to be a less expensive drop-in replacement for Dowex 21K resin. SI-1200 is also a Type I, strong-base resin specifically designed for removal of uranium (ResinTech 2008).

3.1.7 Summary and Recommendations

The 100-HR-3 system has been in operation since 1997, treating groundwater from the 100-D and 100-H Areas. In recent years, total availability has exceeded 95%. Hexavalent chromium removal efficiencies are approximately 95%. Effluent hexavalent chromium concentrations are generally <20 μg/L. The actual capacity of the resin is approximately 1.5% of the theoretical capacity. FH is constructing a test bed to evaluate Dowex 21K and other IX resins under various operating parameters in an effort to extend resin life and reduce O&M costs.

The following recommendations are made for potential operational improvements to optimize the 100-HR-3 IX facility:

- Install a pH meter and recycle pump (or mixer) in the influent storage tank and institute automated pH control with a feedback control loop to remove the two-hour dead time in the current system.

[1] ResinTech® is a registered trademark of ResinTech, Inc. Corporation, West Berlin, New Jersey.

- Examine regenerated resin from Siemens for excessive fine material that would indicate resin damage during the regeneration cycle, shipment, or handling (currently being performed).
- Request that Siemens rinse virgin IX resin with sodium bicarbonate to eliminate acidic effluent during the initial portion of the service cycle (currently being performed).
- In addition to hexavalent chromium, monitor sulfate, nitrate, uranium, and chloride in inter-column and final effluent samples. Assess the potential effects of changes in groundwater constituent concentrations on IX performance.
- In addition to the ResinTech SIR-700 weak-base resin that is already under consideration, evaluate other weak-base anion-exchange resins for potential replacement of Dowex 21K resin.
- Evaluate strong-base and weak-base anion-exchange resin performance under feed pH conditions as low as approximately 5.0 to determine if lowered pH can significantly increase hexavalent chromium loading on the resin (testing of this condition is planned).
- Optimize groundwater extraction to maximize mass removal with minimal hydraulic throughput, taking into account river stage and aquifer rebound effects. This could potentially include suspension of extraction from wells with <20 μg/L hexavalent chromium.

3.2 DR-5 ION-EXCHANGE SYSTEM

The DR-5 IX system was initially installed in the 100-D Area in July 2004 to treat contaminated groundwater contained in the southern part of the northern plume that was not captured by the 100-HR-3 pump-and-treat system. The DR-5 system differs from other systems in the 100 Areas in that the IX resins are regenerated within the system instead of being shipped offsite for regeneration in an effort to reduce O&M costs.

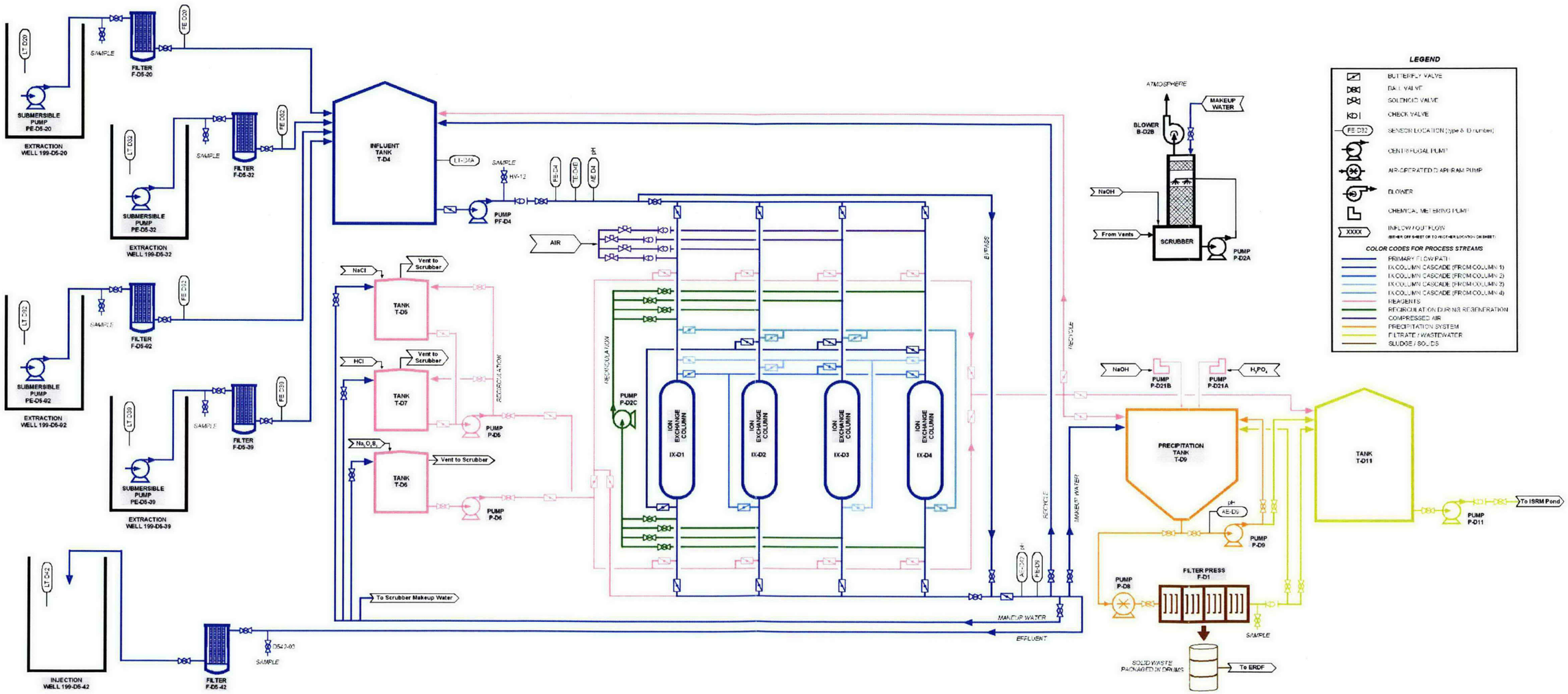
A schematic of the DR-5 IX system is shown in Figure 3-2 (only one of four identical IX columns is shown). It is contained in the 186-D pump-and-treat building, which is located immediately north of the 182-D reservoir and the north end of the ISRM treatment zone (Figure 2-2).

3.2.1 Design Goals/Criteria

Design criteria for the DR-5 system include the following (*Design Basis for the 100-DR-5 Pump and Treat System Design Description* [CP-26710]):

- Treat groundwater at a maximum flow of 189 L/min (50 gpm) with inlet hexavalent chromium concentrations of 200 to 4,000 μg/L
- Generate effluent hexavalent chromium concentrations of <5 μg/L
- Reduce hexavalent chromium to trivalent chromium and stabilize extracted hexavalent chromium and uranium
- Operate unattended and uninterrupted with a 90% total system availability

Figure 3-2. DR-5 Ion-Exchange System).



SOURCE: *DR-5 Process Optimization Study* (HNF-37517 [in publication]).

- Operate within a temperature range of 1.7°C to 38°C (35°F to 100°F)
- Operate at a pressure drop of 3.16 (±0.70) kg/cm^2-d (45 [±10] psid) across the treatment system.

3.2.2 Initial Design

The DR-5 system was designed and constructed by MR3 Systems (DOE/RL-2005-18). The IX system features include the following (*Review of Regeneration of Ion Exchange Resins at DR-5 Pump and Treat Facility to Investigate Process Optimization and Waste Reduction Opportunities* [SGW-36857]):

- Extraction system: Water was originally collected from three extraction wells (199-D5-20, 199-D5-32, and 199-D5-37) using submersible pumps. These wells are located in the northern plume, northwest of the 186-D pump-and-treat building (Figure 2-2). The pipelines from the wells were individually valved to allow adjustment and balance of flows. (Extraction wells were subsequently modified.)
- Influent storage tank: Extracted groundwater is collected in a 11,350-L (3,000-gal) HDPE tank located inside the 186-D pump-and-treat building. The tank contains a level monitor and level switches to prevent tank overflow while maintaining pump operation. A feed pump transfers water to the IX columns at a maximum rate of 189 L/min (50 gpm).
- IX train: Four columns in series each contain 0.79 m^3 (26.7 ft^3) of anion-exchange resin and are valved to allow operation in any sequence. Each column is approximately 0.91 m (3 ft) in diameter and 1.52 m (5 ft) high. The resin occupies 80% of the column volume. At a flow rate of 189 L/min (50 gpm), these dimensions allow for a flow rate of 15 bed volumes/hr across each column.
- Resin: MR3 Systems used a resin that they referred to as MR HCR-48 (DOE/RL-2005-18). According to FH, this resin was procured from Purolite® and is actually A-500, a macroporous, Type 1, strong-base, anion-exchange resin that contains exchangeable chloride ions (Purolite 2008). It has a maximum capacity of 1.15 equivalents/L and can operate at elevated temperatures and a wide pH range. Review of vendor literature suggests that its properties, including pressure drop, are comparable to Dowex 21K resin (Dow 2008).
- Reinjection: Treated water is injected directly from the IX system through well 199-D5-42, which is upgradient of the extraction wells and southeast of the 186-D pump-and-treat building (Figure 2-2).
- Monitoring: The IX system is monitored for influent flow rates, influent and effluent pH, system pressures, and hexavalent chromium concentrations (influent and effluent).

The resin regeneration system features include the following (CP-26710):

- Feed tanks: Regenerant chemicals, sodium chloride, sodium dithionite, and hydrochloric acid are contained in 833-L (220-gal) feed tanks.

Purolite® is a registered trademark of The Purolite Company, Bala Cynwyd, Pennsylvania.

- Precipitation/neutralization tank: Precipitation of chromium and uranium occurs in a cone-bottom reactor. The system includes a 57-L (15-gal) phosphoric acid tank and metering pumps to supply phosphoric acid and sodium hydroxide.
- Filter press: Solids from the precipitation tank are filtered in a 0.085-m^3 (3-ft^3) plate and frame filter press. The press includes an air-assisted hydraulic ram and air blow-down capability.
- Brine holding tank: Liquid streams from the regeneration process are stored in a 5,678-L (1,500-gal) brine holding tank prior to discharge.

3.2.3 System Modifications

The following modifications were made to the DR-5 system during CY05 (DOE/RL-2006-08):

- Extraction well 199-D5-37 was replaced by well 199-D5-92. The extraction rate of the original well was only 11.3 L/min (3 gpm). The replacement well extracts groundwater from the same area but at a higher rate. The average flow in CY06 from well 199-D5-92 was 30.7 L/min (8.1 gpm) (DOE/RL-2007-76).
- Monitoring well 199-D5-39 was converted to an extraction well to capture groundwater from a high hexavalent chromium area south of the 186-D pump-and-treat building.
- Recirculation pumps were added to the IX system to allow recirculation of reagents during resin regeneration and improve regenerant distribution throughout the resin bed.
- The original 3,407-L (900-gal) precipitation/neutralization tank was replaced with a larger 5,678-L (1,500-gal) tank to allow precipitation to be performed in a single step rather than in two batches.

3.2.4 System Operation and Process Description

Groundwater is sequentially pumped from top to bottom through three (i.e., lead, lag, and polish) of the four columns in the system. One of the four columns is always undergoing regeneration or is in standby mode after regeneration is completed. Each of the four columns contains an anion-exchange resin in which chloride ions (Cl^-) are replaced by chromate ions (CrO_4^{-2}). The pressure drop across the system is 3.16 to 3.86 kg/cm^2-d (45 to 55 psid) (SGW-36857) and is a function of system configuration as well as resin type. After treatment, the effluent is either injected into the ground, used for mixing reagent solutions for regeneration, or used as the final rinse during regeneration. Approximately 29,525 L (7,800 gal) of water are used in each regeneration cycle (SGW-36857).

Once a column has been in the lead position for a week, it is taken off-line and regenerated. The weekly frequency of regeneration is based primarily on logistical and operational considerations and is not necessarily based on declining resin performance or breakthrough. Column regeneration is initiated on Mondays to provide adequate time during the workweek for regeneration and waste handling. The remaining columns are cycled as follows: the lag column becomes the lead column, the polish column becomes the lag column, and the previously regenerated column that has been in standby mode becomes the new polish column.

Regeneration is a multi-step process in which the column being regenerated is treated sequentially with three reagents, followed by final rinsing with treated water. Each regenerant solution is recirculated through the column for 10 minutes, followed by a soaking period of 50 minutes. This recycle/soak cycle is repeated three to five times for each regenerant chemical, as described below (SGW-36857):

- Sodium chloride regeneration: A 4-hour (minimum) exposure to a 10% solution of sodium chloride (NaCl) removes adsorbed hexavalent chromium (as CrO_4^{-2}) and uranium (as uranyl carbonate) from the resin.
- Sodium dithionite treatment: A 4-hour exposure to a 14% solution of sodium dithionite ($Na_2S_2O_4$) reduces any residual hexavalent chromium in the resin to trivalent chromium. Reducing residual hexavalent chromium within the resin bed is intended to remove the last remnants of hexavalent chromium from the resin to improve performance as the polishing column. (Trivalent chromium has no affinity for the resin and is easily removed during the hydrochloric acid step, which is next.) Treatment with sodium dithionite is considered time-critical because sodium dithionite has a short shelf life (i.e., it must be used soon after delivery).
- Acid treatment: A five-hour (minimum) wash with a 3% solution of hydrochloric acid (HCl) solubilizes residual trivalent chromium and uranium.
- Rinse: The column is rinsed twice with treated groundwater to remove remaining acidity. A portion of the rinse water is used to fill the precipitation tank to final volume. The remainder bypasses the precipitation tanks and is pumped to the lined retention pond located near the ISRM treatment zone where it evaporates. Water discharged to the ISRM pond must meet a hexavalent chromium limit of 5 mg/L. It has been suggested that this acidic water could be reinjected after pH adjustment.
- Precipitation: Regenerant solutions, as well as a portion of the rinse water from the preceding processes, are treated in the cone-bottom precipitation tank where an 85% phosphoric acid (H_3PO_4) solution is added and the pH is adjusted to 8.5 to 9.0 using sodium hydroxide. Phosphoric acid is added over a 60-minute period, and the sodium hydroxide is added over a 6-hour period. Seed crystals of chromium phosphate ($CrPO_4$) are added prior to addition of phosphoric acid to enhance the quality of the precipitate (*DR-5 Process Optimization Study* [HNF-37517, in publication]). These steps allow the hexavalent chromium to precipitate as chromium phosphate instead of chromium hydroxide [$Cr(OH)_3$] to ensure that the solids will pass the toxicity characteristic leaching procedure (TCLP) criteria and not be considered a hazardous waste.
- Settling: The mixture is allowed to stand for twelve hours to ensure that precipitation and solids settling are complete. Solids are conveyed to a filter press. Wastewater from the precipitation tank is pumped to the ISRM pond to evaporate.
- Filtration: Solids are removed in a filter press for disposal at the ERDF. The chromium concentration in solid waste disposed at the ERDF must be less than the TCLP threshold for chromium. Otherwise, the solid waste must carry the "D007" waste code and meet the non-wastewater land disposal regulations treatment standard of 0.6 mg/L for chromium. Wastewater from the filtration process is pumped to a brine holding tank for ultimate pumping to the ISRM pond.

This regeneration process is more complex than the one used at Siemens for regeneration of Dowex 21K resin (Section 3.1.4). The waste generated from the DR-5 regeneration process includes the following:

- Precipitated solids (including chromium and uranium phosphates): The quantity of sludge generated during each regeneration cycle is approximately 68 L (18 gal) (SGW-36857).
- Precipitation process wastewater: 5,675 L (1,500 gal) per regeneration cycle.
- Final rinse wastewater: 23, 850 L (6,300 gal) per regeneration cycle.

Anionic constituents present in the DR-5 area with the potential to bind to IX resins include nitrate and sulfate. Radionuclides present in the 100 Area in anionic form include uranium [as $UO_2(CO_3)_2^{-4}$] and technetium-99 (as TcO_4^-). Extraction well flow rates and hexavalent chromium and other constituent concentrations measured during fall 2006 (DOE/RL-2007-76) are presented in Table 3-3.

Drinking water MCLs for nitrate and sulfate are 45 and 250 mg/L, respectively. Although anionic forms of uranium and technetium-99 are not contaminants of concern in the DR-5, their presence could affect IX resin performance. Uranium concentrations in 100-D Area groundwater have averaged 1.7 µg/L.

Table 3-3. Flow Rates and Concentrations of Hexavalent Chromium and Other Constituents in DR-5 Extraction Wells (Fall 2006).

Extraction Wells	Flow, L/min (gpm)	Hexavalent Chromium, µg/L	Nitrate, mg/L	Sulfate, mg/L
199-D5-20	28 (7.5)	434	15	47
199-D5-32	57.9 (15.3)	470	30	68
199-D5-39	54.9 (14.5)	1,640	35	75
199-D5-92	31 (8.1)	205	13	32
Overall	**170 (45)[a]**	**790[b]**	**26[b]**	**60[b]**

[a] Total flow.
[b] Flow-weighted average.
gpm = gallons per minute

3.2.5 Operational Performance

Startup of the DR-5 system was initiated in August 2004 and the system became fully operational in December 2004. The operational performance of the system from December 2004 through 2007 is summarized in Table 3-4. Performance data for CY04 through CY06 were obtained from annual summary reports (DOE/RL-2005-18, DOE/RL-2006-08, DOE/RL-2007-76, DOE/RL-2008-05). Regeneration frequencies for CY04 and CY05 were estimated based on total operating hours.

Table 3-4. DR-5 System Operational Performance (December 2004 Through Calendar Year 2007).

	December 2004	CY05	CY06	CY07
Total flow, million L (million gal)	3.4 (0.90)	47.0 (12.42)	81.3 (21.48)	79.3 (20.95)
Total time, hours	730	8,760	8,760	8,760
Planned downtime, hours	7	1,297	172	23
Unplanned downtime, hours	0	1,314	307	182
Total operating time, hours	723	6,149	8,281	8,555
Scheduled availability, percent[a]	100.0	85.0	96.5	97.9
Total availability, percent[b]	99.0	70.2	94.5	97.7
Flow rate, L/min (gpm)	78.3 (20.7)	127 (33.7)	163 (43.2)	154 (40.8)
Flow rate, bed volumes/hour	6.2	10.1	13.0	12.2
Velocity, m/min (ft/min)	0.12 (0.39)	0.20 (0.64)	0.25 (0.82)	0.23 (0.77)
Hexavalent chromium mass, kg (lb)	3.4 (7.5)	38.8 (85.6)	64.6 (142.4)	53.9 (118.8)
Influent hexavalent chromium concentration, µg/L	N/A	837	796	670
Removal efficiency, percent	N/A	99.2	99.9	99.9
Effluent hexavalent chromium concentration, µg/L[c]	N/A	6.7	0.8	0.7
Regeneration frequency, columns/year	4	40	52	52
Hexavalent chromium mass/regeneration cycle, kg (lb)	0.85 (1.87)	0.97 (2.14)	1.24 (2.74)	1.04 (2.29)
Accumulation rate, g/L (lb/ft^3)	1.123 (0.070)	1.281 (0.080)	1.641 (0.102)	1.369 (0.085)
Hexavalent chromium equivalent weight, g/equivalent	26.0	26.0	26.0	26.0
$Capacity_{actual}$, equivalents[d]/L	0.043	0.049	0.063	0.053
$Capacity_{theoretical}$, equivalents/L	1.15	1.15	1.15	1.15
Capacity fraction, percent[e]	3.76	4.29	5.49	4.58

[a] Scheduled availability = 100 x (total available time-unplanned downtime)/total available time.
[b] Total availability = 100 x (total available time-total downtime)/total available time.
[c] Effluent hexavalent chromium concentration = influent concentration x removal efficiency.
[d] Equivalents are units of negative charge carried by anions .
[e] Capacity fraction = 100 x (actual capacity/theoretical capacity).
CY = calendar year
N/A = not applicable

During the period from December 2004 through CY05, 50.4 million L (13.3 million gal) of groundwater were treated and 42.2 kg (93.1 lb) of hexavalent chromium were extracted. During this period, the effluent hexavalent chromium concentrations exceeded 50 µg/L on two occasions and exceeded the RAO limit (20 µg/L) on several additional occasions. The total availability of the system during CY05 was 70% because of significant downtime while the system was modified, as previously discussed in Section 3.2.3.

After the extraction well changes (Section 3.2.3), the average annual flows in CY06 and CY07 were approximately 80 million L (21 million gal). Average flow rates were 159 L/min (42 gpm). The average total availability was 96%. The average influent hexavalent chromium concentration during this period was 733 μg/L. The average annual hexavalent chromium mass removed was 59 kg (131 lb). Effluent hexavalent chromium concentrations have been below the RAO limit since the beginning of 2006 and have also been below the target of 5 μg/L since June 2006. Removal efficiencies exceeded 99% during CY06 and CY07.

As previously noted, the resin in the lead column is regenerated weekly without regard to column performance. During CY06 and CY07, the average quantity of hexavalent chromium removed during each operating cycle was 1.1 kg (2.5 lb). The average quantity of hexavalent chromium captured on the lead column before regeneration was 5.0% of the theoretical capacity.

Since the DR-5 system has been in operation, a total of 211 million L (56 million gal) of groundwater have been processed and 161 kg (354 lb) of hexavalent chromium have been removed from the groundwater. The hexavalent chromium removal efficiency has averaged 99.7%. The system has operated for approximately 23,500 hours without replacement or addition of resin. Scheduled availability has been 93%. The DR-5 system has met the current design criteria under normal operating conditions, treating groundwater flows of up to 189 L/min (50 gpm) with influent hexavalent chromium concentrations ranging from 200 to 4,000 μg/L, while producing effluent concentrations <5 μg/L with only few exceptions. The IX system operated unattended (except during regeneration) within the required temperature range at a pressure of 3.16 (±0.7) kg/cm^2-d (45 [±10] psid).

The resin in each column has been regenerated approximately 37 times since initial installation. Purolite A-500 resin is reported to have a life of 3 to 5 years, thus it could be near the end of its useful life, and it has been indicated by FH personnel that resin breakdown products might be appearing in the effluent. There are no data on resin capacity in the DR-5 system or the impact of nitrate, sulfate, or uranium compounds on performance.

The installation of a regenerant recycle system, increased precipitation tank volume, and pH adjustment improved hexavalent chromium removal from the loaded resin and has allowed longer final rinse times. Recently, the Washington State Department of Ecology expressed concern that the hexavalent chromium concentration in the filter press filtrate placed in the ISRM pond exceeded the 5 mg/L limit. It was found that the hexavalent chromium concentration decreased significantly after filtering through a 0.45-micron filter, demonstrating that particulate hexavalent chromium was responsible for the high concentration. Accordingly, the settling time in the precipitation tank was increased to 48 hours and the total hexavalent chromium concentration fell to <2 mg/L.

3.2.6 Process Optimization Status

The process optimization goals for the regeneration/precipitation system include the following (HNF-37517):

- Reduce regeneration processing time and chemical usage.
- Reduce wastewater volumes conveyed to the ISRM pond.

- Ultimately comply with the goal of eliminating discharge of wastewater to the ISRM pond. The goal would be to send solid waste to the ERDF and reinject all treated wastewater.

In CY08, FH performed bench testing to improve the efficiency of the resin regeneration and trivalent chromium precipitation and removal processes. The work indicated that phosphoric acid use could be reduced from a 400% stoichiometric excess to a 15% stoichiometric excess. Adjusting the pH to between 10.0 and 10.5 greatly reduced the time required for chromium phosphate precipitation and settling, and also reduced turbidity in the aqueous phase after settling of solids. Investigators are using a step-wise approach to modify the process with an interval for evaluation after performance of each step. The following steps have been completed:

- Reduced phosphoric acid to a 15% excess
- Raised the pH to between 10.0 and 10.5 after phosphoric acid is added
- Added $CrPO_4$ seed crystals after pH adjustment instead of after phosphoric acid addition
- Reduced settling time to 12 hours, which ultimately reduced the total chromium effluent to < 0.2 mg/L.

Steps remaining to be performed include the following:

- Increase the rate of sodium hydroxide addition in order to reduce the time for pH adjustment to one hour
- Increase the filtering time.

3.2.7 Summary and Recommendations

The unique feature of the DR-5 system is the onsite regeneration/precipitation system. The Purolite A-500 resin has similar characteristics to the Dowex 21K resin used at other systems in the 100-D Area. The system has been operated since December 2004 without significant downtime, except when the system was modified during CY05. Since then, the system has met all design goals, with the exception of unattended operation of the regeneration system. The resin has not been replaced since the system was installed.

Fluor Hanford, Inc. has initiated optimization of the regeneration and precipitation processes to reduce O&M costs and to reduce generated quantities of solid waste and wastewater. The following recommendations for future optimization programs focus on waste minimization:

- Complete the optimization program that is under way.
- Neutralize the acidic rinse waters from the last cycles of column regeneration with magnesium hydroxide or sodium bicarbonate, either of which provides pH buffering. Inject the buffered solutions along with the treated groundwater.
- Investigate the use of polyelectrolytes to improve precipitate settling rates and solids capture in the filter press.

- Replace the regeneration process with the process used at the Siemens facility in Roseville, Minnesota (Section 3.1.4). The resin would be regenerated with sodium chloride and chromium would be reduced in the precipitation tank instead of on the IX column.
- Evaluate hexavalent chromium reduction with sodium metabisulfite instead of sodium dithionite. Hexavalent chromium could be reduced with sodium metabisulfite on the IX column or in the precipitation/neutralization tank. Unlike oxidation-sensitive sodium dithionite, sodium metabisulfite does not degrade during storage.
- As an alternative to sodium metabisulfite, evaluate hexavalent chromium reduction using ferrous chloride. Hexavalent chromium would be reduced in the precipitation/ neutralization tank at an approximate pH of 6.8, followed by air oxidation of residual ferrous iron at an approximate pH of 7.8.
- Introduce sodium hydroxide to a slurry of seed crystals before its addition to the precipitation/neutralization tank. The presence of seed crystals when sodium hydroxide is added will promote formation of larger crystals of chromium phosphate that will settle and dewater more readily.
- If hexavalent chromium can be reduced in the precipitation/neutralization tank, evaluate treating the high strength sodium chloride regenerant solution with a small nanofiltration membrane system. A nanofiltration membrane solution will reject divalent ions such as chromate and sulfate. The resulting brine could be augmented with fresh sodium chloride and used in subsequent regeneration cycles. This could allow more economical disposal using the wiped-film evaporator that is reportedly available at Hanford.
- If the volume of concentrated waste streams can be sufficiently reduced by recycling regenerants, evaluate metered co-injection with treated water.
- Evaluate hexavalent chromium reduction using ferrous chloride (or sulfate) as a replacement for the existing IX process, taking into consideration solid and liquid waste generation, and regulatory factors.
- Optimize groundwater extraction to maximize mass removal with minimal hydraulic throughput, taking into account river stage and aquifer rebound effects.

3.3 OPERATIONAL COST EVALUATION AND COMPARISON OF THE 100-HR-3 AND DR-5 SYSTEMS

Table 3-5 compares operating costs for the DR-5 system with the 100-HR-3 system during CY05 through CY07 (DOE/RL-2006-08, DOE/RL-2007-76, DOE/RL-2008-05). Table 3-6 presents the fractional costs for each operational cost category. Operating cost elements include the following (DOE/RL-2008-05):

- Design: Design activities for system construction, upgrades, and modifications.
- Project support: Project coordination and technical consultation as required during design, construction, acceptance testing, and operation.
- O&M: Costs associated with facility operations, routine field screening and engineering support, and periodic maintenance.

- Performance monitoring: System and groundwater sampling and chemical analysis in accordance with relevant interim action work plans.
- Waste management: Cost for management of spent resins in accordance with applicable laws and waste designation sampling and analysis. It also includes costs for resin regeneration and purchase of new resins.

Table 3-5. Comparison of DR-5 and 100-HR-3 System Costs (Calendar Years 2005 Through 2007).

Cost or Operational Item	DR-5	100-HR-3
Design cost	$544,000	$368,000
Project support cost	$1,197,000	$1,820,000
Operation and maintenance cost	$1,607,000	$2,355,000
Performance monitoring cost	$119,000	$1,307,000
Waste management cost	$228,000	$873,000
Total cost	$3,696,000	$6,723,000
Hexavalent chromium processed, kg (lb)	157 (347)	88.4 (195)
Water treated, million L (million gal)	208 (54.9)	1,035 (273)
Operating time, hour	22,985	25,384
Cost per kg (lb) of hexavalent chromium	$23,443 ($10,656)	$75,885 ($34,493)
Cost per million L (million gal)	$17,769 ($67,332)	$6.496 ($24,626)
Cost per hour	$161	$265

Table 3-6. Calendar Years 2005 Through 2007, System Costs (Percent of Total).

Cost Category	DR-5	100-HR-3
Design,	14.7	5.5
Project support	32.4	27.1
Operation and maintenance	43.5	35.0
Performance monitoring	3.2	19.4
Waste management	6.2	13.0
Total	**100.0**	**100.0**

It is of limited usefulness to directly compare costs of the DR-5 and 100-HR-3 systems because the 100-HR-3 system treats higher flow rates of groundwater with lower hexavalent chromium concentrations, while the DR-5 treats lower flow rates of groundwater with higher hexavalent chromium concentrations. Accordingly, the DR-5 system has a lower cost per unit mass of hexavalent chromium treated and a higher cost per unit volume of water treated compared to the 100-HR-3 system. It also has a lower cost per hour because it is a smaller system (the DR-5 system's total cost is about half that of the 100-HR-3 system even though it has removed almost twice as much hexavalent chromium). This information suggests a possible advantage of targeting groundwater extraction to the most contaminated zones, since higher concentrations are

more cost effectively treated. However, the difference in resin and the presence of other constituents (e.g., uranium) could also contribute to the lower cost per unit volume for the DR-5 system. Efforts to optimize groundwater pump-and-treat systems at the 100-D Area should, thus, consider targeted groundwater extraction, as well as more efficient ex situ treatment.

Despite the above-mentioned differences between the two systems, O&M cost is the largest cost category for both systems, suggesting that efforts to optimize O&M could be advantageous. Project support is the second largest cost category for both systems.

3.4 ELECTROCOAGULATION TREATABILITY INVESTIGATION

Electrocoagulation has been proposed as a potential alternative to the existing IX process for removing hexavalent chromium from groundwater in the 100-D Area. Electrocoagulation was believed to offer several advantages over IX, including reduced cost and increased operational simplicity. Another point of interest for electrocoagulation is that it does not increase the dissolved solids concentration of the treated water, as occurs with more conventional chemical precipitation processes.

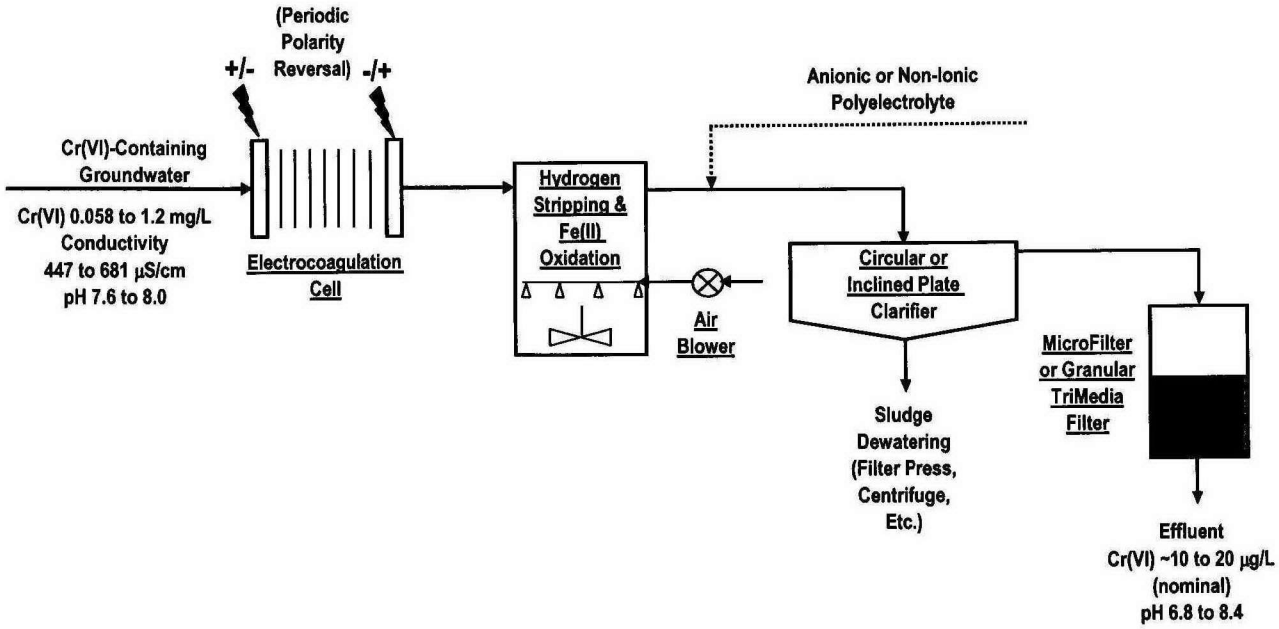
Pilot testing was carried out at the 100-D Area for the purpose of determining the effectiveness of hexavalent chromium removal and verifying the robustness, implementability, and scalability to larger size of the electrocoagulation process. The work plan identified the performance objective of reducing the hexavalent chromium concentration in treated water to 20 μg/L or less. The test was set up to provide the contractor maximum flexibility to demonstrate the technical feasibility of the process, but they encountered technical difficulties and were unable to achieve all the objectives. In addition, the plan identified five operational objectives (*Treatability Test Report for the Removal of Chromium from Groundwater at the 100-D Area Using Electrocoagulation* [DOE/RL-2008-13, in publication]):

- Determine the volume and composition of waste streams and their proper waste designation
- Determine whether the system could operate in an unattended mode
- Evaluate the reliability and safety of the process
- Assess the overall treatment cost per unit volume of groundwater treated
- Obtain data for potential scale-up of the process to larger hydraulic capacity.

3.4.1 Process Overview

Electrocoagulation has been used for a wide variety of disparate applications, such as rendering plant wastewater, treating grain-based food manufacturing wastewater, and removing hexavalent chromium. A generalized process schematic for a system to treat hexavalent chromium is shown in Figure 3-3.

Figure 3-3. Schematic Diagram of Electrocoagulation System Process.



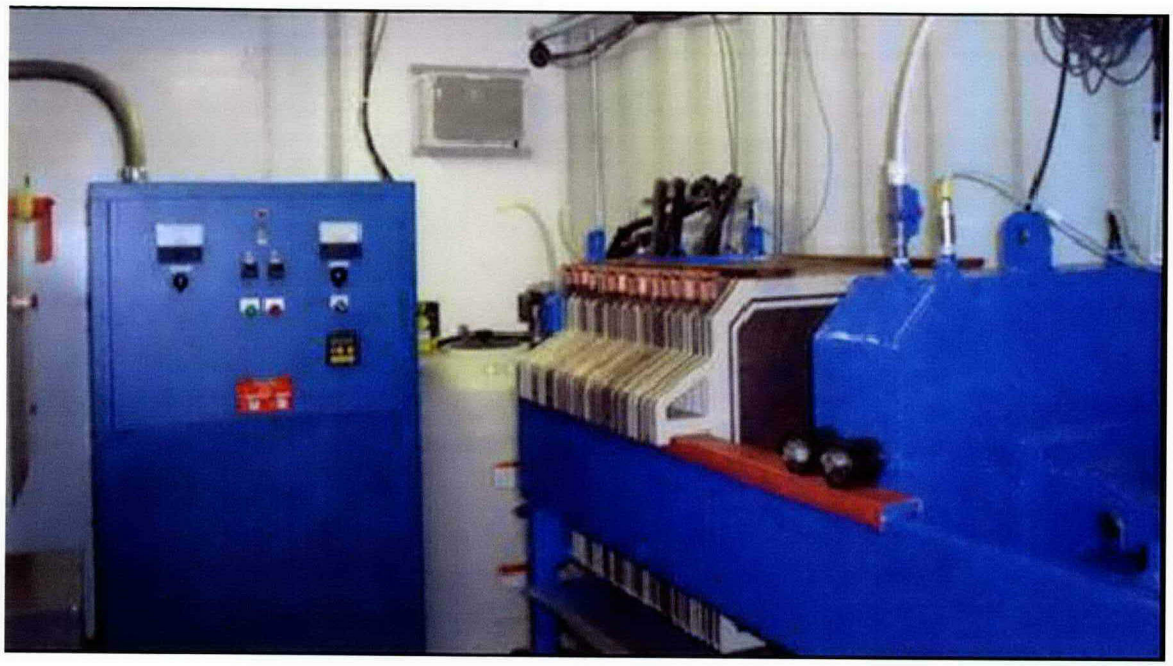
Reduction of hexavalent chromium by divalent iron [Fe(II)] produces trivalent chromium and trivalent iron [Fe(III)], both of which form insoluble hydroxides at groundwater pH values. In electrocoagulation, Fe(II) is generated electrolytically by oxidation of a sacrificial iron or steel anode. In chemical reduction, Fe(II) is added in the form of soluble salts, such as ferrous chloride ($FeCl_2$) or sulfate ($FeSO_4$). Both reduction processes require downstream oxidation of residual Fe(II) and filtration of solids. Electrocoagulation requires stripping of hydrogen gas, which is generated at the cathode, to prevent an explosive condition.

There is limited standardization for electrocoagulation design for hexavalent chromium treatment applications. Actual treatment efficiency is often determined empirically, after plant startup. With few basic design principles to draw upon, process scale-up from small-scale tests needs to be performed carefully, with an understanding that test results with equipment from one manufacturer are not necessarily transferable to equipment from another manufacturer. After 100 years, the process still needs a systematic, comprehensive approach to understand key mechanisms and factors controlling electrocoagulation performance ("Electrocoagulation as Wastewater Treatment" [Holt et al. 1999]).

3.4.2 Pilot Electrocoagulation Cell Operation

Pilot testing was performed at a nominal flow rate of 189 L/min (50 gpm) for the period May through October 2007, with groundwater containing hexavalent chromium at concentrations of approximately 200 to 250 µg/L. The pilot electrocoagulation unit is shown in Figure 3-4. The unit contained a stack of 27 steel plate electrodes with dimensions of 61 cm by 61 cm by 0.64 cm (24 in. by 24 in. by 0.25 in.). Electrodes were separated in the frame by 0.6 cm (0.25 in.). During operation, the polarity of the plates was reversed periodically to reduce surface fouling and to equalize rates of plate metal loss.

Figure 3-4. Electrocoagulation Unit with Plate-and-Frame Construction.



For the first four days of operation, the electrocoagulation unit reduced hexavalent chromium to <10 μg/L while operating at 4 to 6 volts, with a current of 60 to 70 amps, and an estimated current density of 1.4 to 1.6 amps/m^2 (15 to 17.5 amps/ft^2).

With ongoing operation, however, effluent hexavalent chromium concentrations increased, which prompted increases in cell current that finally peaked at above 600 amps during the period of July through October 2007 (Figure 3-5). The initial current efficiency was approximately 1.8% at 60 amps, but it later decreased to 0.18% as the current rose to 600 amps. Current efficiency is defined at the actual quantity of hexavalent chromium reduced compared to the theoretical quantity that could be reduced.

Pilot testing showed that the hexavalent chromium concentration could be reduced below the 20 μg/L treatment goal, but not consistently. Effluent hexavalent chromium concentrations ranged from approximately 2 to 70 μg/L (Figure 3-6).

During operation, anodic surfaces become scaled with iron oxide (mainly ferric hydroxide [$Fe(OH)_3$] and magnetite [Fe_3O_4]), which passivated the electrodes (i.e., made them less reactive), necessitating increased current to sustain hexavalent chromium reduction. At the cathode, alkaline scale (likely calcium carbonate) formed. Anode passivation and cathode scaling were addressed by periodically reversing cell polarity, causing the cathode to become acidic, dissolving alkaline scale, and the anode to become alkaline, evolving large amounts of hydrogen, which, in principle, dislodge iron-oxide scale deposits.

Figure 3-5. Electrocoagulation Cell Voltage and Amperage During Pilot Testing.

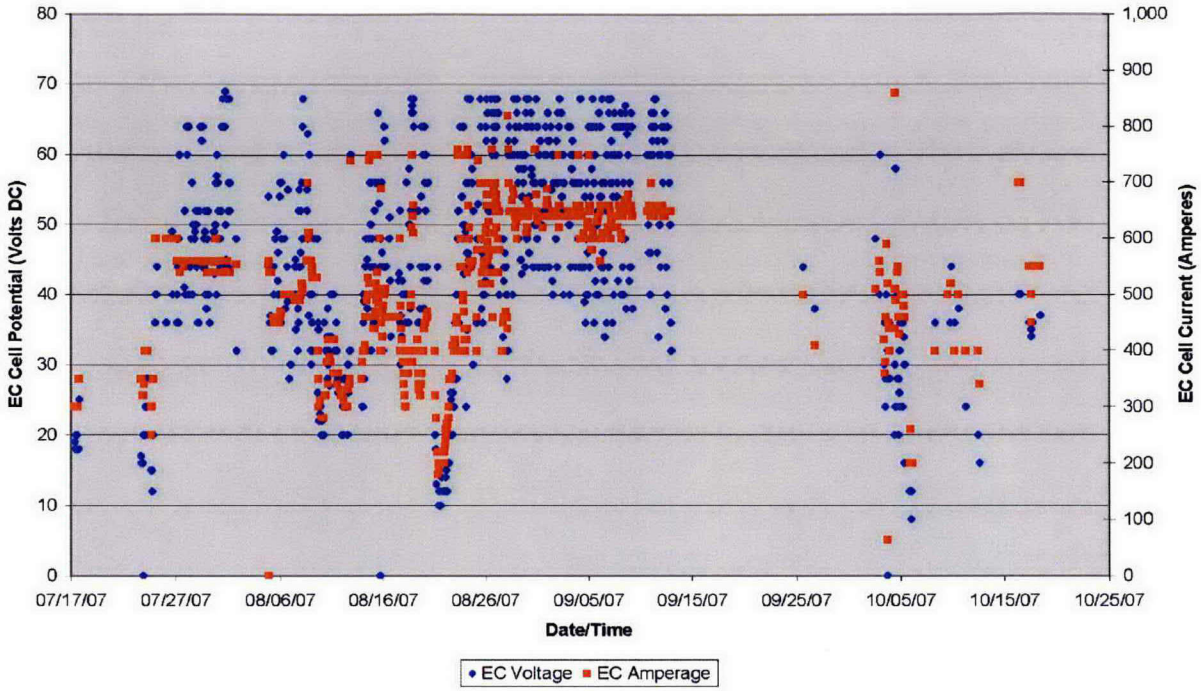
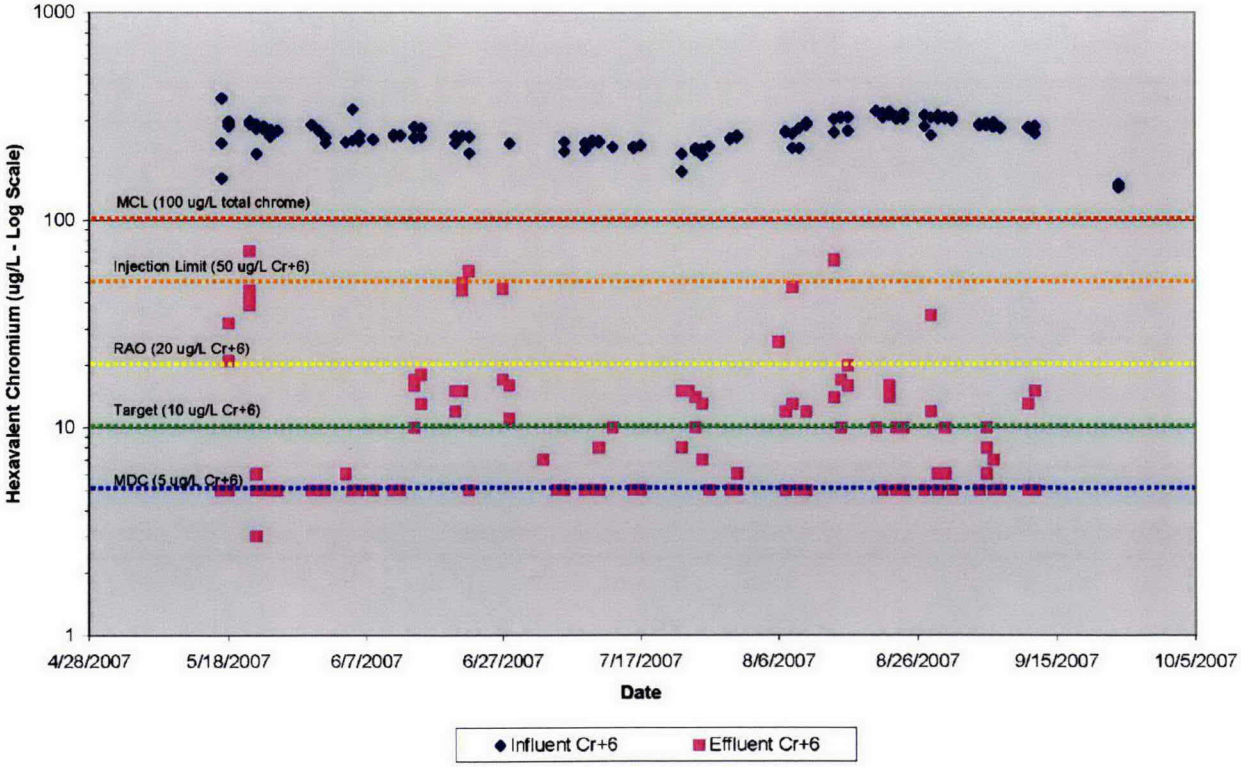


Figure 3-6. Hexavalent Chromium Influent and Effluent During Pilot Testing.



Preliminary inquiries had shown that most manufacturers adjust the polarity reversal frequency based on field operating experience, with typical intervals ranging from 15 to 60 minutes. Loose interpretation of the test data suggests that operation at relatively low current density and with more frequent cell polarity reversal might reduce passivation and scaling.

Magnetite that formed on the anode tended to be adherent and, after extended periods of operation, it needed to be mechanically removed from the electrodes. This was labor-intensive and resulted in operational downtimes lasting 6 to 8 hours. It is strongly recommended that any future electrocoagulation unit be equipped with a set of spare electrodes to replace those being mechanically cleaned.

Magnetite, which is a semi-conductor, also tended to dislodge from the electrode surfaces and short-circuit the cell. An attempt was made to clean magnetite from the anode surfaces by raising the current to 700 amps for short period of time. This effort led to short-circuiting and forced a plant shutdown. Inspection of the electrodes showed that tuberculation created bridges between electrodes, which short-circuited the cell, as shown in Figure 3-7.

3.4.3 Summary and Recommendations

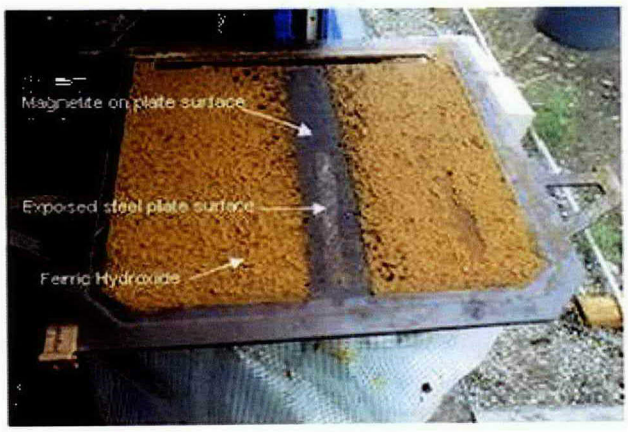
As noted above, the work plan identified operational objectives. Based on pilot testing, the following can be concluded with respect to operational objectives:

- Electrocoagulation was able to reduce hexavalent chromium to below 2 μg/L, but only when electrodes were clean, provisionally meeting the overall performance objective.
- Wastes from the process passed toxicity and corrosivity criteria, and with process modifications unrelated to the electrocoagulation process, should pass the "paint filter" test.
- The electrocoagulation unit was unable to operate unattended, failing to meet a key operational objective.
- Excluding injection well maintenance, subcontracted technical support, overhead and burden, the estimated cost to treat groundwater during the test was $0.21/L ($0.78/gal). This is approximately 10 to 20 times the cost of IX treatment at the 100-D Area (Section 3.3).
- The data obtained during pilot testing were not sufficient for scale-up to larger hydraulic capacity without further engineering assessment.

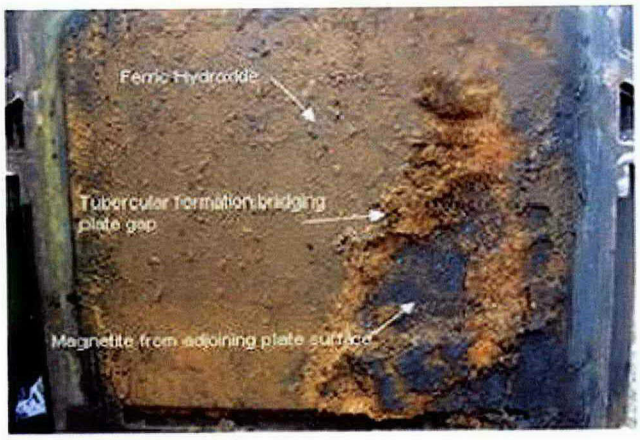
Other significant results included the following:

- The initial current efficiency was approximately 1.8% at 60 amps, but after electrode passivation progressed, the current efficiency fell to 0.18% as the current increased to 600 amps.
- Operation at high current density (16.3 amps/m^2 [175 amps/ft^2], approximately 10 times the initial current density) was ineffective for "burning" the passive layer off the electrodes.
- Anode cleaning with hydrochloric acid was ineffective and did not restore cell performance. Labor-intensive mechanical cleaning was required.

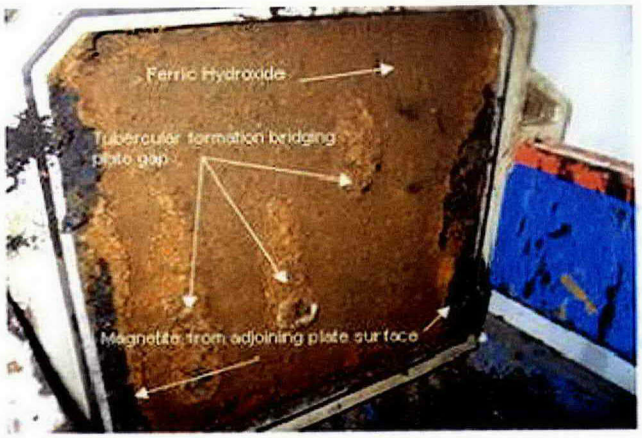
Figure 3-7. Electrocoagulation Electrode Fouling.



a. EC cell electrode plate fouling observed on 29 June 2007. Plate removed from EC cell. Ferric hydroxide and magnetite have been scraped from surface as indicated.



b. EC cell electrode plate fouling observed on 20 August 2007. Plate removed from EC cell.



c. EC cell electrode plate fouling observed on 11 October 2007. Plate in position in EC cell.

The following recommendations are made if electrocoagulation is to be pursued further:

- Electrocoagulation as a technology has few basic design principles to draw upon for process design purposes, so pilot testing must be performed with equipment from the manufacturer who will provide the full-scale system.
- Carefully planned fundamental investigations into the electrocoagulation process are needed to provide a firm technical basis for design and predictable performance.
- Low current density and 30- to 60-second polarity reversal cycles should be investigated as a means of reducing electrode passivation and improving performance.
- Groundwater pH should be reduced to control or prevent alkaline scaling.
- Spare sets of electrodes should be available to minimize system downtime for cleaning magnetite and alkaline scale from used electrodes.

4.0 SUMMARY OF THE HEXAVALENT CHROMIUM TREATMENT TECHNOLOGY EXCHANGE MEETING

As part of the overall RPO effort for the 100-D Area, a technology exchange meeting was held on April 8 through 10, 2008, in Richland, Washington, to review remediation technologies applicable to hexavalent chromium. The goal of this meeting was to enable RL and FH staff to obtain detailed information on potential technologies applicable to the full-scale remediation of hexavalent chromium-contaminated groundwater for the 100 Areas in general and the 100-D Area in particular. Information was presented by a panel of nine scientists and engineers who were primarily consultants to private industry (as well as one scientist from DOE's Pantex Plant). Practitioners in both ex situ and in situ treatment were included on the panel, as well as individuals knowledgeable about chromium chemistry and biochemistry. The list below identifies the panelists, their affiliations, and presentation titles:

- Dr. Bruce Wielinga, Geomatrix Consultants, Inc., *Environmental Chromium Biogeochemistry*
- Dr. Chad Seidel, P.E., DSWA, *Chromium Treatment Research for Drinking Water Application*
- Mr. Jim Mavis, P.E., CH2M Hill, Inc., *Reductive Ex Situ Treatment Technologies*
- Mr. Ron Borrego, P.E., Geomatrix Consultants, Inc., *Ex Situ Treatment Alternatives Based on Discharge Options*
- Mr. Chris Lyles, DOE Pantex, *Chromium Treatment of Groundwater at the DOE Pantex Plant*
- Dr. Thomas Simpkin, P.E., CH2M Hill, Inc., *Overview of Pneumatic Injection of Zero-Valent Iron for In Situ Hexavalent Chromium Reduction*
- Mr. Jim Rouse, MWH Americas, Inc., *In Situ Injection and Infiltration of Calcium Polysulfide*
- Mr. Jim Harrington, P.E., Alexco Resources, *In Situ Bioremediation*
- Dr. Ernie Stine, Shaw Environmental, *In Situ Bioremediation and Calcium Polysulfide Case Studies*.

This section presents a summary of this meeting and is directly excerpted, with very minor revisions, from a report prepared by Geomatrix Consultants that summarizes this technology exchange meeting[1].

The meeting agenda included (1) presentations by the DOE, FH, and Pacific Northwest National Laboratory on Hanford activities related to remediation of hexavalent chromium in groundwater; (2) a field trip to the 100 Areas; (3) panelists' presentations; and (4) an informal discussion.

[1] An informal report, *Chromium Treatment Technology Information Exchange for Remediation of Chromium in Groundwater at the Department of Energy Hanford Site*, was prepared by Geomatrix Consultants, Inc. and submitted to Fluor Hanford, Inc., which summarizes the technology exchange meeting that was held in Richland, Washington, April 8-10, 2008.

A technical report was prepared by the panelists that summarizes each of their presentations on remedial projects for treatment of hexavalent chromium in groundwater, including some discussion of their potential applicability at Hanford (see footnote 1 on previous page). This report was not a consensus document, but presented individual viewpoints and experiences. The subsections below attempt to highlight salient points from the technical report that are directly applicable to Hanford hexavalent chromium treatment issues.

4.1 CHROMIUM CHEMISTRY, CHROMIUM BIOGEOCHEMISTRY, AND OTHER CONSIDERATIONS

A number of the panelists discussed chromium chemistry, chromium biogeochemistry, and other considerations that could impact remedial design at Hanford. Because chromium can exist in two different oxidation states in the environment, either +6 (hexavalent) or +3 (trivalent), and because the trivalent state is less mobile (i.e., less soluble) and less toxic, many treatment technologies are based upon reduction of the hexavalent form to the trivalent form with subsequent removal or immobilization. Trivalent chromium usually is incorporated into a ferric-chromium oxyhydroxide precipitate. Common reductants with the capability of reducing hexavalent chromium to the trivalent form include the following:

- Aqueous ferrous iron (either as ferrous sulfate or ferrous chloride solution)
- Solid zero-valent iron
- Reduced sulfur (added as calcium and/or sodium polysulfide, hydrogen sulfide, sulfite, metabisulfite, or dithionite)
- Micro-organisms (supplied with an organic carbon substrate or an inorganic source of electron donor).

Chemical mechanisms are believed to be much more rapid than biological mechanisms. However, when considering the stoichiometric reactions for biological versus chemical treatment, it appears that the biological reduction is more efficient in terms of molar requirements. For example, one mole of sodium lactate in biological reduction reduces four moles of hexavalent chromium, while three moles of calcium polysulfide in chemical reduction are required to reduce two moles of hexavalent chromium (an efficiency difference of 6:1 for biological reduction as compared to chemical reduction). This efficiency may relate to overall treatment system cost, and so, may be important during alternatives evaluation. However, in a field application, comparison of molar efficiencies becomes complicated by the fact that the reductant is treating all reducible species (e.g., nitrate and dissolved oxygen), not simply hexavalent chromium, and there are numerous other factors critical to the selection of reducing amendments, as discussed further below.

At some sites, the best option may involve a combination of both chemical and biological amendments. Various amendments may also be applied in different locations of a plume, such as at the source area versus the distal portions of the plume, and in the vadose zone versus the saturated zone.

Previous technical reviews of treatment technologies for hexavalent chromium in groundwater in the 100-D Area identified issues that may impact remedial design:

- For in situ treatment applications, physical and chemical heterogeneity of the aquifer materials in the 100-D Area must be considered in the design of the treatment system
- In situ and ex situ treatment design must consider the presence of other constituents, such as nitrate and oxygen, which may (1) require much larger quantities of treatment reagents be added, because of increased electron demand[1], or (2) produce wastes that may require special handling (e.g., radioactive materials), or (3) result in the release of other metals, such as manganese or arsenic, because of the change in reduction-oxidation conditions.

Because both chemical and biological mechanisms for reduction of hexavalent chromium will likely follow the same chemical reaction pathway and require contact between reagent and contaminant, technology selection should be partially based upon criteria such as safety, ease of use, byproduct production, and cost. For example, when comparing calcium polysulfide to biological treatment, the sulfide treatment may result in the deposition of a considerable mass of elemental sulfur and calcium carbonate, whereas the biological treatment will add alkalinity, carbon dioxide, and biomass.

Some of the panelists favor in situ remedial approaches because they deem them to be more efficient than ex situ approaches. Others recognize the benefits of pump-and-treat systems for hydraulic control of the contaminant plume and removal of contaminant mass. Many of the case studies presented in the report involve sites where pump-and-treat systems had been operational for many years before an in situ treatment approach was implemented due to lack of remedial progress with the pump-and-treat approach. Specifics of delivery approaches, including details such as well spacing and types of amendments delivered, are presented in the case studies. Several of the panelists believe that at Hanford a plume-wide in situ treatment approach, including vadose zone source treatment, could achieve remedial goals within several years, whereas pump-and-treat alone will likely require decades of operation. This is based upon their experience at sites similar to Hanford. They also state that no single approach works for every site, but each site must tailor the remedial approach, especially amendment delivery, to site-specific conditions.

4.2 EX SITU TECHNOLOGIES FOR TREATMENT OF HEXAVALENT CHROMIUM IN GROUNDWATER

The presentations describing experience with ex situ treatment of hexavalent chromium in groundwater focused on drinking water applications based upon bench- through full-scale study of multiple technologies, reductive ex situ treatment technologies, and consideration of alternatives based upon discharge options.

Bench-scale testing of various ex situ technologies for drinking water applications involved the following technologies; their relative performance is also noted below:

- Adsorption (9 media): poor to excellent
- IX (5 resins tested): excellent

[1] At the In Situ Redox Manipulation barrier in the 100-D Area, >99% of the reductant is consumed by oxygen and nitrate present in the groundwater.

- Membrane treatment (nanofiltration, reverse osmosis, and ultrafiltration): poor to excellent
- Reduction and precipitation: good.

Pilot testing of the above technologies for drinking water applications identified three technologies as leading candidates for demonstration-scale testing:

- Strong-base, anion-exchange resin
- Weak-base, anion-exchange resin (two of six outperformed others in testing: ResinTech SIR-700 and Duolite® A7)
- Reduction, coagulation, and filtration.

It is the opinion of the panelists involved in this work that Hanford may not be operating the existing pump-and-treat systems under optimal conditions, thus experiencing higher operational costs than necessary; improvements would extend the time between resin regeneration cycles and minimize waste production. Further recommendations were for onsite bench- or pilot-scale testing of current market-available strong-base anion and weak-base anion resins and comparison to reduction/coagulation/filtration to determine the best solution for specific Hanford conditions. (Note that an onsite resin testing plan has been prepared, and a resin test skid is being procured for testing various resins.)

Reductive ex situ treatment technologies presented at the workshop include sulfur dioxide and its derivatives (sulfite/metabisulfites, and sulfite), ferrous iron compounds, electrocoagulation, zero-valent iron, and ferrous sulfide.

- Sodium metabisulfite has been used widely since before the mid-1930s for industrial applications, but it is not recommended for Hanford ex situ application because the reaction is too slow, unless the pH is reduced to below 3.0. Other potential issues may include effects of residual sulfur in the aquifer. Polysulfide has recently been used for ex situ treatment of extracted groundwater prior to reinjection into the aquifer.
- Ferrous chloride or ferrous sulfate treatment is effective, inexpensive, and rapid but generates four times the sludge mass as that of reduced sulfur compounds.
- One benefit of electrocoagulation is that it does not introduce anions into the treated water system. However, testing at Hanford demonstrated potential operational issues with electrode passivation and cathode scaling (Section 3.4).
- Zero-valent iron requires acidification of the influent groundwater prior to treatment to overcome coating of the media with ferric hydroxide, but the acidic conditions also promote dissolution of the zero-valent iron itself. It is not recommended for ex situ treatment.
- Ferrous sulfide is not currently used for chromium treatment for safety reasons and thus is likely not well suited for application at Hanford.

Duolite® is a registered trademark of Dow Chemical – Rohm and Haas Company, Philadelphia, Pennsylvania.

Selection of ex situ treatment technologies must include consideration of a number of factors, which include discharge options, groundwater ownership, waste generation, schedule, longevity of the treatment system, permitting requirements, and cost, among other factors. Ex situ technologies described as alternatives in this section of the report include: coagulation/filtration, IX, reverse osmosis, lime softening, electrochemical precipitation using ferrous iron, electrodialysis reversal/electrocoagulation, adsorption/chelation, and biological treatment. Each of these options is described in terms of performance and waste generation.

Reinjection of the treated water must include consideration of the chemistry of the treated water, chemistry of the receiving groundwater, the mineralogy of the aquifer materials, and regulatory approval. The following recommendations were made regarding the reinjection of treated water after ex situ treatment:

- Treated water should be filtered before reinjection, preferably with a microfilter or mixed media filter, which should be selected based upon the type of treatment technology and the injection well construction and maintenance program.
- pH adjustment may be required to avoid plugging of the aquifer, depending upon the selected reagent.

4.3 IN SITU TECHNOLOGIES FOR TREATMENT OF HEXAVALENT CHROMIUM IN GROUNDWATER

The two keys to successful remediation of chromium in groundwater via in situ methods are (1) selection of the appropriate amendment based upon the aquifer geochemistry and mineralogy, and (2) selection of the appropriate reagent delivery method based on site hydrogeologic conditions. In situ reduction using biological and chemical treatment has been applied to full-scale treatment of hexavalent chromium in groundwater at numerous sites. These technologies can be used to treat source zones or dissolved plumes, or to provide a barrier using injection wells. The amendments are delivered to the subsurface as dissolved reagents in injected fluid or as solids, typically in an atomized slurry. Other in situ amendments have been used for treatment of hexavalent chromium, including sodium dithionite at Hanford and gaseous hydrogen sulfide in the vadose zone at the White Sands Missile Range. The most mature in situ biological and chemical reduction technologies were discussed by several of the panelists at the treatment technology exchange meeting and are summarized below.

These in situ technologies allow high-dose amendments to be delivered to the aquifer at any depth to which a borehole can be drilled. The biggest uncertainty and challenge with their application lies with the actual distribution of the amendment in the subsurface, which will largely determine the overall success of the remediation. Further information on amendment delivery approaches is provided in Table 4-1. Table 4-2 describes features of three in situ treatment technologies: bioremediation, reduced sulfur addition, and zero-valent iron addition. All three technologies have been proven to reduce hexavalent chromium in groundwater, and all can be used alone or in combination with others.

Table 4-1. Delivery Technologies Considered for In Situ Treatment System Design.

Technology	Design Considerations	Applicability at Hanford
Injection/extraction (i.e., recirculation systems): • Well to well • Basin to well • In-well (not considered for aquifers <30 ft thick)	Delivery via boreholes as wells or uncased, drilled by conventional or direct-push methods. Delivery across screen zone or depth-discrete injection to address heterogeneity. Recirculation systems can use existing pump-and-treat systems or can be designed separately. Recirculation systems can use various geometries (e.g., extract from core of plume and inject on edges or extract downgradient) and inject upgradient in source area. Does not treat the vadose zone.	Conversion of Hanford pump-and-treat to active recirculation system as well as source/distal plume configurations should be considered. Surface infiltration at source should be considered as part of recirculation system. Must consider downgradient impacts on river (may require injection of air or oxygenated water in a line parallel to the river to prevent flow of reduced groundwater into the river).
Infiltration galleries (e.g., pits, basins, trenches, or pipe grids)	Good alternative that avoids plugging of injection wells in recirculation systems. Downgradient groundwater treatment system should be emplaced in conjunction with infiltration system. Treats the vadose zone source.	Believed to be very appropriate for Hanford conditions; however, requires demonstration.

Because these in situ technologies induce a reductive target zone, they have many of the same strengths and weaknesses. Those shared in common include the following:

- They will consume nitrate.
- They will also consume other constituents, such as oxygen.
- They can be applied to plume treatment, upgrade of the ISRM barrier, creation of a new barrier, or infiltration in source areas within the vadose zone.
- They may release other constituents of potential concern, such as manganese or arsenic.

4.4 CONCLUSIONS AND KEY SITE UNCERTAINTIES

The presenters and meeting attendees generally agreed that the optimization of the current pump-and-treat systems and/or incorporation of new treatment media may provide cost and performance benefits. However, there was also a general consensus that treatment of the hexavalent chromium plume in the 100-D Area with pump-and-treat technology alone would require many decades of treatment. To expedite the remediation process, a more aggressive holistic approach that uses both ex situ and in situ technologies to address both the groundwater and the vadose zone is recommended. In situ reduction of hexavalent chromium can be readily accomplished with either chemical or biological approaches, or a combination thereof, and there are a variety of potential methods for delivering reductive amendments. Whichever approach or combination of approaches is ultimately implemented, it will be important to achieve hydraulic control to ensure protection of the Columbia River and avoid potential impacts to the current pump-and-treat systems that are in place to contain the plume.

Table 4-2. Selected In Situ Remediation Technologies.

Technology/Amendment	Emplacement Mechanism	Design Considerations	Strengths/Weaknesses	Cost	Performance
Bioremediation (liquid amendment) substrates may include the following: • Alcohols • Organic acids • Sugar syrups • Vegetable oils • Other organic substrates. Each has advantages and disadvantages.	Typically done on a wide injection well spacing.	Presence of additional contaminants must be considered, as they could impact longevity of reducing capacity; other additional contaminants may accumulate in the reducing zone. Bench-scale testing may be done to enable selection of the best substrate for a specific site.	May take longer to treat than chemical because of slower kinetics. Potential plugging of formation with biomass or carbonates.	Low-cost amendment may result in cost advantage, but many factors must be considered.	Performance can be enhanced in reduced zones by creating recirculation gradients, possibly using existing pump-and-treat systems.
reduced sulfur compounds (liquid amendment): • Calcium polysulfide (liquid amendment) • Ferrous sulfide • Sodium metabisulfite. Other sulfur-based chemicals, such as sodium dithionite, are available.	Typically done on a wide injection well spacing.	Can combine with addition of carbon source to prevent production of excess sulfate. Must consider other constituents that will use the electrons, such as oxygen and nitrate, in designing the treatment system.	Potential plugging of formation or piping with sulfates or carbonates. Potential increases in sulfate in groundwater.	Higher unit cost amendment.	Estimate 1.5 pore volumes of amended water must be pumped and reinjected to achieve hexavalent chromium remediation.
Zero-valent iron. Micron-scale or nano-scale solid particles. Gas injection followed by atomized slurry in newly drilled boreholes.	Depends upon formation character: • Dispersion (coarse materials) • Fluidization (coarse materials) • Fracture filling (fine-grained materials).	Effect of other reducible compounds (e.g., oxygen and nitrate), and release of potential contaminants due to change in reduction-oxidation state.	Strong reductant can be added as high dose. Exposure to oxygenated waters could produce ferric oxide coatings on the iron particles.	$9 to $37/kg ($4 to $17/lb) of zero-valent iron emplaced.	Results from 12 sites, depths from <35 to 100 ft below ground surface: • Approximately 70% good distribution • Approximately 63% good performance • Approximately 50% were fractured.

The following uncertainties were identified during the meeting and it was generally agreed that they should be addressed prior to or during the RI/FS process planned for the 100-D Area:

- Contaminant sources are only partially defined and must be addressed in remedial design.
- Hexavalent chromium plumes are not fully delineated laterally or vertically.
- The flux of water through the vadose zone has not been determined, thus adding uncertainty to surface infiltration as an approach. An infiltration test could be conducted to improve this understanding.
- Groundwater/surface water interactions are not fully understood and need to be considered in regard to potential re-oxidation of reduced species, seasonal impacts, and the requirement for dissolved oxygen concentrations of at least 6 mg/L in near-river monitoring wells.
- Heterogeneity of the aquifer may impact the strength and longevity of the reduced zones and must be considered in the remedial design.
- Lower permeability units or stringers may serve as long-term sources of hexavalent chromium and thus could impact remedial effectiveness and timelines.
- Contaminated groundwater currently impacting the river may require more immediate attention, possibly using different technologies, than groundwater that is further inland.

5.0 TECHNOLOGY SCREENING AND DECISION ANALYSIS

The interim remedial actions implemented at the 100-D Area were primarily designed to protect the river by intercepting downgradient portions of the plumes and eliminating the discharge of hexavalent chromium to the river at concentrations >20 μg/L. Although the existing systems have reduced the levels of hexavalent chromium discharging to the river, they have not been able to eliminate hexavalent chromium exceedances at the river, nor have they been able to reduce the concentrations and extent of hexavalent chromium contamination in the upgradient areas of the plumes to the extent anticipated. As stated in Section 2.0, these systems were never intended for, nor are they capable of, addressing secondary sources of hexavalent chromium in the vadose zone that are continuing to feed the plumes. Unless additional actions are taken to accelerate the cleanup of the residual source areas and plume hot spots, it may be necessary to operate the existing systems for decades. Any future RAAs with the potential to accelerate remediation and closure of the site will likely be comprised of both in situ and ex situ remedial components. Consequently, the identification and evaluation of potential new or alternative remedial technologies is an important part of the 100-D Area RPO process.

A technology screening meeting was held for planning purposes on June 4 through 6, 2008, in Richland, Washington, and facilitated decision analysis was employed to assist with the identification, screening, and ranking of potential remedial technologies that are appropriate for the 100-D Area. This was an internal project team meeting with an objective of developing a list of applicable technologies. Each technology was evaluated in terms of strengths and weaknesses as it relates to the 100-D Area and its unique challenges.

The following activities were accomplished during the decision analysis session and are consistent with the RPO effort for the 100-D Area remediation system:

- Working RAOs were developed for the 100-D Area for planning purposes
- Weighted screening criteria were developed with which to compare and screen technologies
- A brainstorming session was used to identify an array of prospective technologies for the screening process
- The prospective technologies were screened and ranked using the criteria.

Subsequent to the DA, those technologies that scored relatively high in the screening process were combined to create a range of RAAs with the potential to achieve the working RAOs for the 100-D Area (Appendix A). As discussed in Section 1.0, these alternatives will be screened and FS-level designs and costs will be developed for the preferred alternative(s) in the fall of 2008.

5.1 WORKING REMEDIAL ACTION OBJECTIVES

Before discussion of potential technologies, the decision analysis meeting participants agreed that it was appropriate to articulate working RAOs so everyone was considering and evaluating the technologies in the context of achieving RAOs. These working RAOs are thought to meet or

exceed the protectiveness of the existing interim RAOs and, subject to revision, may be used for the final ROD.

Two working RAOs were identified for the 100-D Area and are summarized below:

1. Immediate protection of the aquatic receptors in the Columbia River. The group concurred that the term "immediate protection" means that all applicable standards are to be met in the river no later than 2012.
    a. This includes meeting the standard of 10 μg/L for hexavalent chromium in the river. The regulatory agencies have determined that a 1:1 mixing factor is appropriate at the 100-D Area. Therefore, 100-D Area groundwater adjacent to the river (which will seep into the river and become mixed with river water) may contain up to 20 μg/L of hexavalent chromium.
    b. This also includes meeting a standard of at least 6 mg/L of dissolved oxygen in groundwater adjacent to the river.
    c. All other groundwater parameters will need to be sufficiently protective of the river such that the river water complies with all other applicable requirements.
2. Achieve remediation goals for all groundwater at the 100-D Area by 2020.
    a. This includes meeting a standard for hexavalent chromium in groundwater some distance upgradient of the river (values for the standard and the distance to be determined by modeling), so as to be protective of the river according to the standards above.
    b. This also includes meeting the MCL of 100 μg/L for total chromium throughout the plume.
    c. Meeting the goals for hexavalent and total chromium will require continued management of the vadose zone in order to restore and protect groundwater.

5.2 MULTI-ATTRIBUTE VALUE ANALYSIS

A multi-attribute value analysis was used to establish a hierarchy of decision criteria. Criterium DecisionPlus™ Version 3.0 software was used to facilitate brainstorming, calculate results, and present results of the screening. The team conducted a brainstorming session to develop the criteria that should be considered in the decision-making process.

The primary criteria for screening technologies replicates EPA interim guidance (*Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLS, Interim Final* [EPA/540/G-89/004]), which recommends screening technologies based on effectiveness, implementability, and cost. Each of these Level 1 criteria has subordinate criteria, and the team thought would be useful to better characterize the Level 1 criteria. Two Level 2 criteria also had subordinate criteria (technical and administrative implementability).

Criterium DecisionPlus™ is a trademark of Integrated Software Solutions, LLC, of Seattle, Washington.

In all, a total of 15 different criteria were brainstormed (Figure 5-1). Some of these criteria were subordinate to others. Taking this into account, each technology was screened against 10 final screening criteria (see highlighted yellow boxes in Figure 5-1). Figure 5-1 shows the relative weights of each of the criteria, as determined by the meeting participants. The weighting of the ten highlighted criteria ranged from 7.5% to 15% of the total weighting (100%); thus, no one criterion dominated the decision process, and no one criterion was weighted so low that the contribution could be considered negligible.

5.2.1 Technology Brainstorming

The meeting attendees determined that four different groups of technologies needed to be evaluated:

- Technologies that can address the first RAO of immediately protecting the river
- Technologies that can address the vadose zone
- Groundwater remediation technologies
- Ex situ groundwater treatment technologies.

It was anticipated that many RAAs would ultimately need to include one or more technologies from each of these categories. The focus was on hexavalent chromium. It will be important to ensure that selected remedies will also meet applicable standards for other constituents and parameters.

After the above four categories of technologies were defined, the group brainstormed technologies to identify (without judgment) any and all possibilities for remedial technologies that could be employed at the site to achieve the working RAOs. The group then pared the list to remove those technologies that were deemed too expensive, untested, ineffective, or otherwise unacceptable to warrant serious consideration.

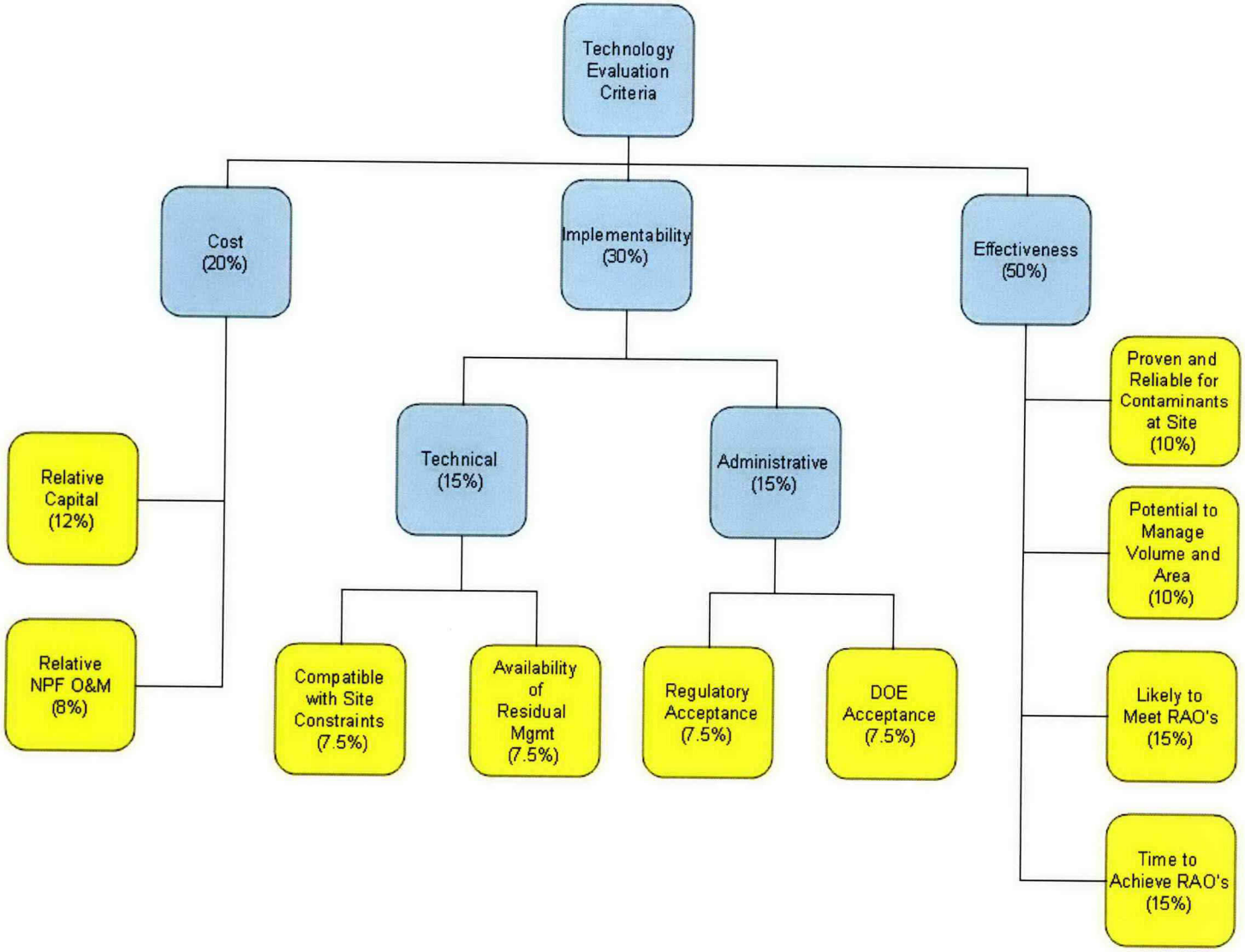
If consensus was not reached on eliminating a given technology, it was retained for screening so as not to eliminate any technology that could possibly be viable. The technologies that survived the initial cut are described in Sections 5.2.1.1 through 5.2.1.4, and they are listed in order of eventual scoring, from high to low favorability.

5.2.1.1 River Protection Technologies Retained for Screening.

- Biological barrier(s): Periodic injection of a carbon substrate (electron donor) would create and maintain a reducing zone perpendicular to groundwater flow, causing the dissolved hexavalent chromium to be reduced and precipitated prior to reaching the river. This technology would require an ancillary technology to re-oxygenate groundwater before discharge to the river.

- Hydraulic barrier using injection at river (mounding): A series of wells or trenches, or a horizontal well, would be used to inject uncontaminated water to the area adjacent to the river for at least part of the year. If vertical wells were used, it is anticipated that the installation of a minimum of 40 to 50 wells would be required to cover the length of the potential plume interface with the river. Regardless of the infiltration or injection technology used, the injection rate would need to be sufficiently high to create a slight mound in the underlying water table. The injected water could include either groundwater or river water, or a combination of both.

Figure 5-1. Value Hierarchy and Criteria Weighting for Technology Screening.



- Air sparging: Air would be injected in a series of air sparging wells to re-oxygenate groundwater before discharge to the river. (This would be an ancillary technology as air sparging could not be used to remediate hexavalent chromium as a stand-alone technology.)
- Chemical barrier(s): This is similar to biological barrier(s) described above but would involve injection of a chemical reducing agent rather than a carbon substrate.
- Plume interception: Groundwater would be extracted prior to discharge to the river using a series of wells. (The water would then be treated using one of the ex situ treatment technologies described later.)
- Gradient control: This is similar to plume interception described above but would involve more aggressive groundwater extraction to maintain a hydraulic gradient from the river inland toward the 100-D Area groundwater on a year-round basis.
- Continue all current actions: Operation and upgrade of the ISRM would be continued. (This would likely be an ancillary river protection technology because it alone is not achieving the river protection working RAO.)
- Phytoremediation: A large number of deep-rooted trees would be planted next to the river to uptake contaminants and provide a hydraulic gradient from the river inland.
- Offsets: Salmon redds (spawning grounds) would be created somewhere else rather than protecting the river at the 100-D Area. The new redds could theoretically result in the same or improved net environmental benefit since they could increase the salmon population.

5.2.1.2 Vadose Zone Technologies Retained for Screening.

- Biological infiltration: Groundwater from extraction wells would be amended with a carbon substrate and injected via drip lines, sprinklers, or infiltrators (i.e., in a leachfield-type configuration) above a contaminated vadose zone. Micro-organisms would consume the carbon substrate and create reducing conditions whereby the hexavalent chromium would be reduced and precipitated. Feet (meters) per day of water migration can take place in the vadose zone, which generally does not become fully saturated. Treatment times of 6 to 12 months are possible.
- Chemical infiltration: This is similar to biological infiltration but would use a chemical reduction amendment rather than a carbon substrate. Treatment effects would be more instantaneous. There is a potential for increased mobilization of constituents.
- Remove, treat, and dispose: Contaminated soil would be excavated and disposed at the ERDF after appropriate treatment.
- Water flushing: Contaminated portions of the vadose zone would be flushed with water, carrying hexavalent chromium down to the groundwater where it would be subsequently addressed using one of the groundwater remediation technologies described later.
- Continue all current actions: Excavation of hot spots in the vadose zone would continue under the current program of Washington Closure Hanford, LLC.

- Aggressive injection with pump-and-treat: This is similar to water flushing above but would use higher water flow rates in the vadose zone coupled with more localized groundwater extraction and treatment beneath and immediately downgradient of the vadose zone area being treated.
- Institutional controls: Contaminated portions of the vadose zone would be prohibited from certain uses (such as residential) rather than being remediated to soil RAOs.
- Gas-phase injection: Hydrogen gas (or organic gas, such as propane) would be injected into the vadose zone to serve as an electron donor for autotrophic micro-organisms to use for the reduction of hexavalent chromium to trivalent chromium.
- Vegetated (evapotranspiration) cap: A vegetated soil cap would evapotranspire precipitation falling on the area before it could infiltrate and leach hexavalent chromium from contaminated soils and carry it to groundwater.
- Containment and isolation: Contaminated soil would be encapsulated to prevent contact with water and receptors.
- Surface barrier: An impermeable barrier would be placed on the ground surface above contaminated soils to prevent infiltration of precipitation and leaching and transport of hexavalent chromium to groundwater.
- Grouting/solidification: Contaminated soils would be grouted or solidified in place to prevent hexavalent chromium from leaching from them.

5.2.1.3 Groundwater Treatment Technologies.

- In situ biological treatment: A carbon substrate would be injected into groundwater throughout the plume for micro-organisms to consume, thereby creating reducing conditions that would convert hexavalent to trivalent chromium.
- In situ chemical treatment: This is similar to in situ biological treatment but a chemical reductant rather than a carbon substrate would be used.
- Reactive biological barrier: This is similar to in situ biological treatment but carbon substrate would be injected in one or more barrier configurations rather than throughout the plume.
- Reactive chemical barrier: This is similar to in situ chemical treatment, but a chemical reductant would be injected in one or more barrier configurations rather than throughout the plume.
- Expand the existing pump-and-treat system: Additional extraction wells would be installed and the groundwater extraction rate would be increased.
- Continue all current actions: Groundwater extraction and treatment would continue using the existing system.
- Water flushing: Surface or shallow subsurface discharge of treated effluent in targeted areas where secondary contamination is present would increase the rate that hexavalent chromium is flushed out of the vadose zone. The resulting increased groundwater contamination would be captured and treated and then returned to the discharge area to complete the cycle.

- Zero-valent iron injections: Zero-valent iron would be injected into the saturated zone, either throughout an area or in a barrier configuration. Hexavalent chromium would be reduced to trivalent chromium as zero-valent iron is oxidized to ferrous and/or ferric iron.
- Institutional controls: Groundwater would be prohibited from being used for certain purposes, such as for drinking water.
- Monitored natural attenuation (MNA): MNA would track the disappearance of hexavalent chromium in time and/or space under the action of a variety of natural processes.

5.2.1.4 Ex Situ Groundwater Treatment.

- Optimize existing systems: IX would continue to be used, but different resins and O&M strategies would be tested to find ways to optimize treatment and reduce costs.
- Reinfiltration with biological amendments: Rather than treating the extracted groundwater in an engineered facility, the extracted groundwater would be amended with a carbon substrate and reinjected into the subsurface for treatment to take place there. Biological reduction would take place in the vadose prior to the injected water reaching the water table.
- Ferrous iron reduction: Ferrous iron salts would be used to reduce hexavalent chromium. Post- reduction aeration, flocculation/settling, and filtration would be part of the treatment train to remove excess ferrous iron and solids generated. This technology is commonly used to treat metals in electroplating wastes (see Section 6.0 for a more detailed discussion).
- Continue all current actions: IX treatment would continue to be used as in the past.
- Reinfiltration with chemical amendments: This is similar to reinfiltration with biological amendments but a chemical reductant would be used instead of a carbon substrate.
- Bioreactor treatment: Extracted groundwater would be treated in an ex situ bioreactor. Various types of bioreactors could be used including fluidized beds, floating beds, membrane bioreactors, and membrane biofilm reactors.
- Reverse osmosis: Pressure forcing water through a membrane would filter out the hexavalent chromium and other ions.
- Phytoremediation: Extracted groundwater would be used to irrigate plants. Root exudates serve as a carbon and energy source for micro-organisms to create reducing conditions and reduce hexavalent chromium to trivalent chromium.
- Constructed wetlands: An area would be lined, filled with a substrate layer of wood chips or similar material, and planted. Water would be introduced via a series of pipes, and plants would be grown to generate enough carbon to be self-sustaining. Hexavalent chromium would be removed by direct uptake in plants or reduced in biologically created reducing zones, and trivalent chromium would adsorb to the substrate material.

- National pollutant discharge elimination system discharge: Groundwater, either treated or untreated, would be discharged to the river via diffusers. If allowed by the regulatory agencies, much higher treatment standards could be obtained since mixing of the groundwater with the river water could provide significant reductions in the concentrations of groundwater constituents. Additional treatment or engineering controls may be warranted if fouling of injection delivery systems is possible.
- Sulfur-modified iron treatment: Granular media would be used to remove hexavalent chromium by adsorption or by reduction to trivalent chromium followed by precipitation of Cr_2O_3.
- Sulfide treatment: Ferrous sulfide would be added to the water to chemically reduce hexavalent chromium to trivalent chromium, with the concurrent precipitation of chromium hydroxide and ferric hydroxide and conversion of sulfide to sulfate,
- Send to an existing treatment plant: A pipeline would be constructed and untreated groundwater would be pumped to the 200 Area Effluent Treatment Facility.
- Electrocoagulation: Direct current applied across iron electrodes would produce ferrous iron that would reduce hexavalent chromium in groundwater. This process would result in the formation of trivalent chromium and trivalent iron that would co-precipitate as insoluble hydroxides at the appropriate pH. (See Section 3.4 for a description of an electrocoagulation pilot test at the 100-D Area.)

5.2.2 Technology Scoring

Rating spreadsheets were created based on the value hierarchy presented in Figure 5-1. The attendees (listed in Appendix B) then individually rated the surviving technologies against the screening criteria.

Meeting attendees individually scored the 45 technologies described above against the 10 screening criteria. Some people worked together as a group and produced a single score representing the group. Thus, a single scoring sheet would include 450 values. Scorers were instructed to generally use values of 25, 50, or 75 (or low, medium, and high) to represent how well a technology met the decision criteria. Several people used intermediate values. Values of 0 and 100 could also be used (to denote 100% negative rating and 100% positive rating, respectively). If an individual was unfamiliar with a technology, the corresponding scoring spaces could be left blank and these cells would then not enter into the calculations.

A total of 11 score sheets were completed during the decision analysis session, and each of the 11 scores was assigned the same weight. All of the results were either directly entered into a Microsoft Excel® worksheet, or entered on paper and then entered into a Microsoft Excel worksheet. The worksheets were then compiled into a single workbook so the average scores could be calculated from all the worksheets. These scores were then entered into the Criterium DecisionPlus software to calculate the normalized score of each technology. Results are presented in Figures 5-2 through 5-5, for river protection, vadose zone treatment, groundwater treatment, and ex situ treatment technologies, respectively.

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Figure 5-2. Composite Scores for River Protection Technologies.

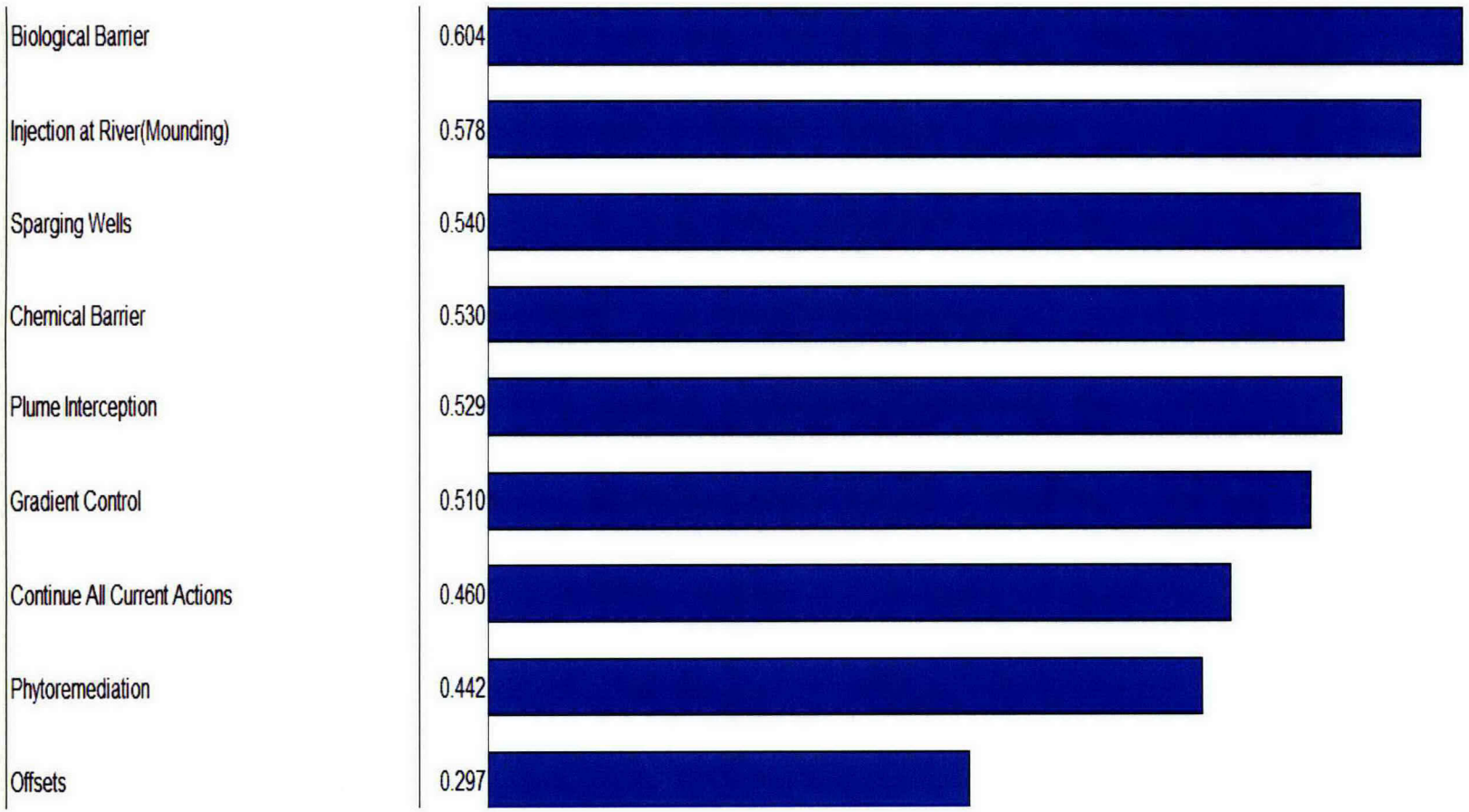


Figure 5-3. Composite Scores for Vadose Zone Treatment Technologies.

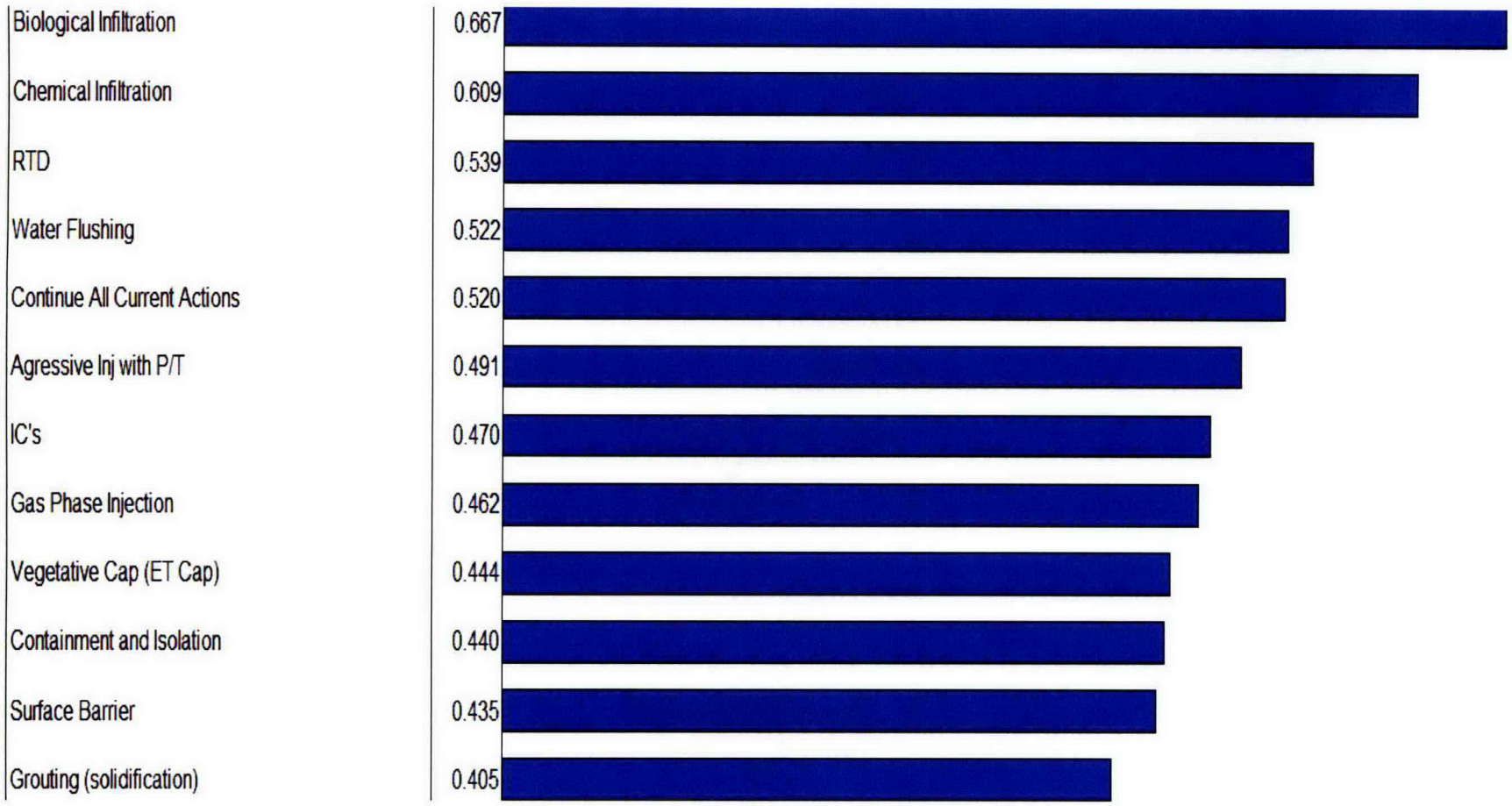


Figure 5-4. Composite Scores for Groundwater Treatment Technologies.

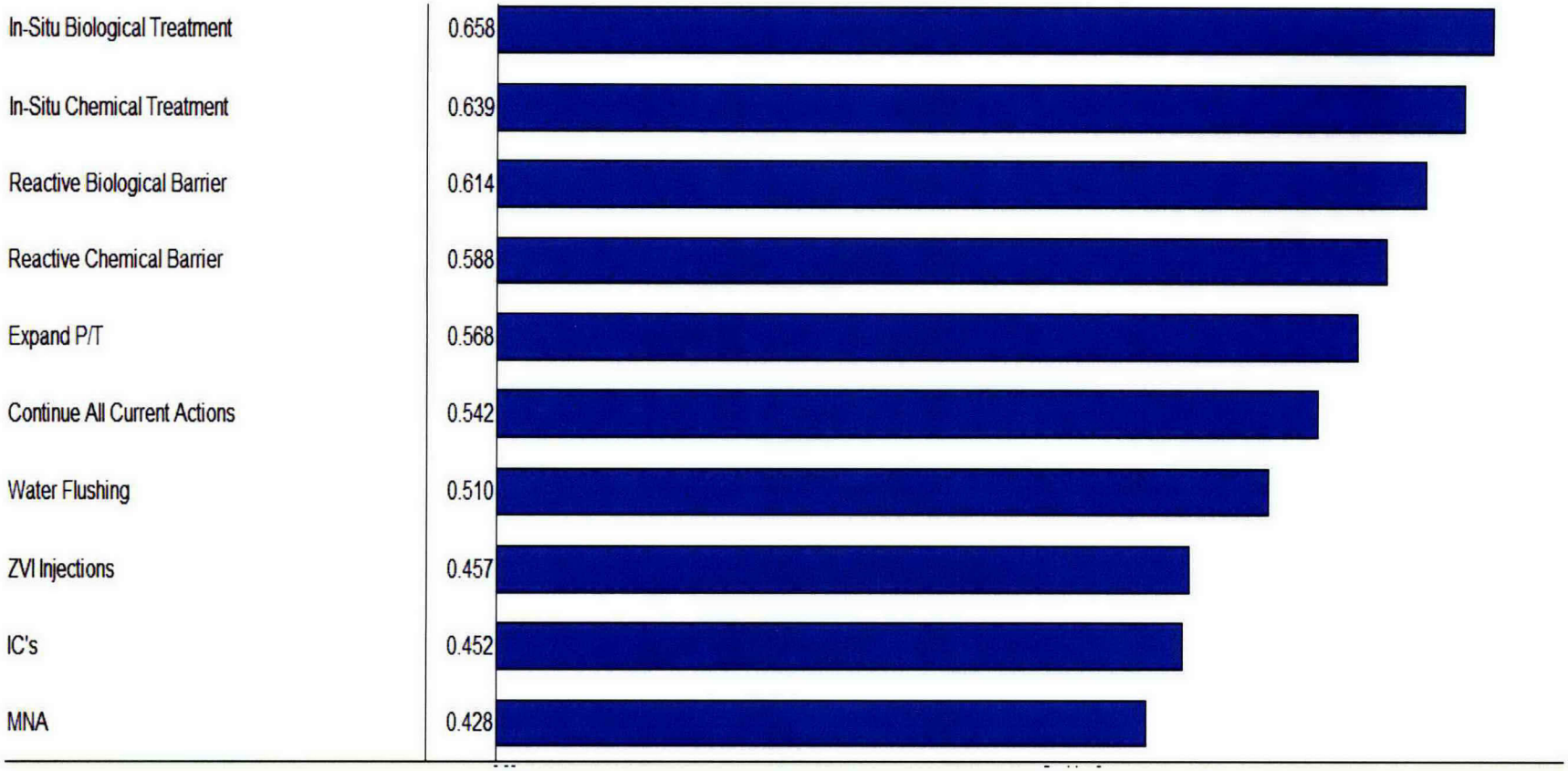
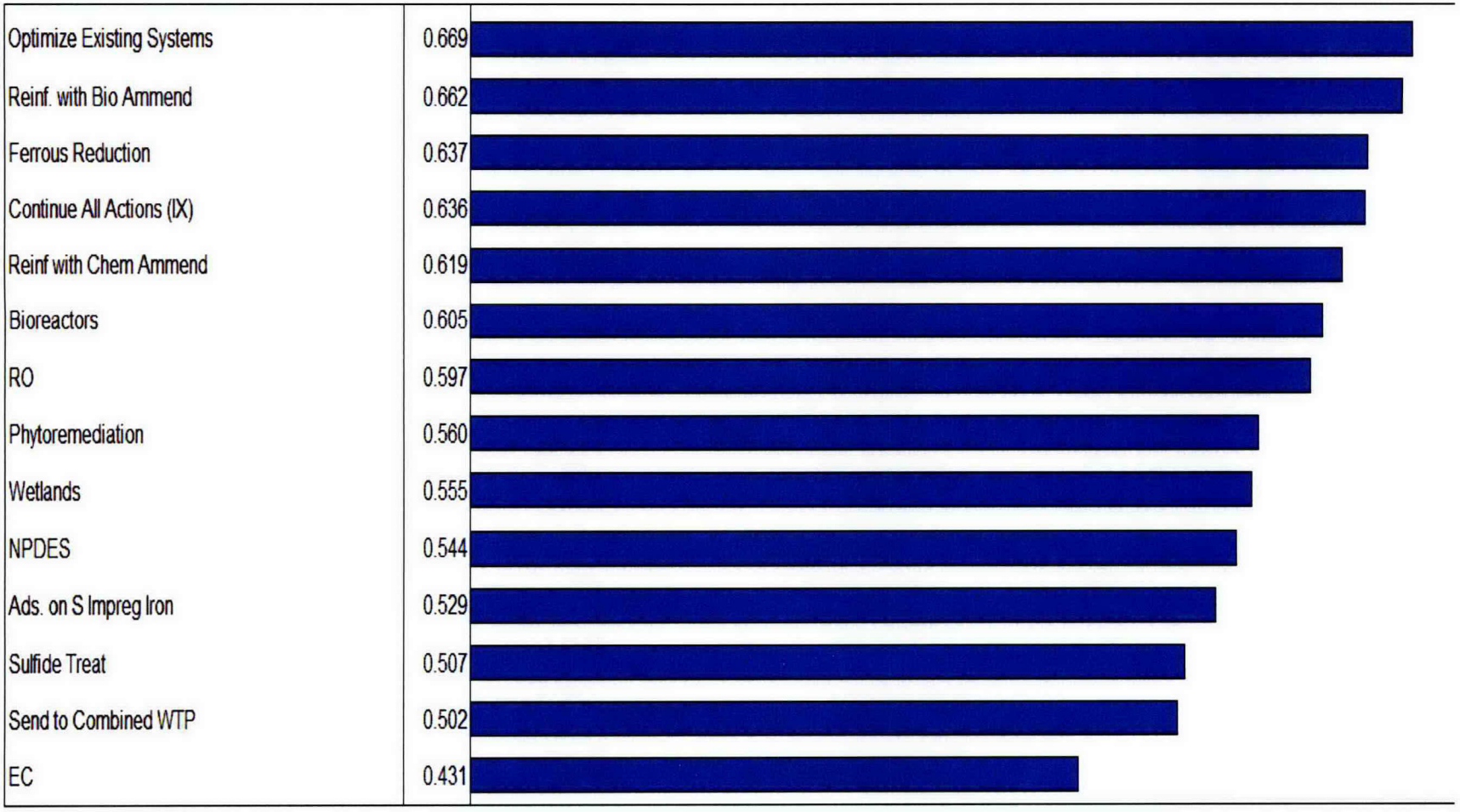


Figure 5-5. Composite Scores for Ex Situ Treatment Technologies.



In reviewing the scores, several observations were noted:

- Biological technologies tended to be highly scored, followed closely by chemical technology counterparts.
- The top-scoring river protection technologies were biological barrier, followed by hydraulic barrier using injection at river, sparging wells, and chemical barrier. Because sparging wells are an ancillary rather than stand-alone technology, this option should not be compared directly with the others. Injection at river could either be ancillary or stand-alone.
- Top-scoring vadose zone technologies were biological infiltration, followed by chemical infiltration, remove/treat/dispose, and water flushing.
- Top-scoring groundwater treatment technologies were in situ biological treatment, followed by in situ chemical treatment, in situ biological barrier, and in situ chemical barrier.
- Top-scoring ex situ groundwater treatment technologies were optimize existing systems, followed by re-infiltration with biological amendments, ferrous iron reduction, and continue all actions (keep using IX as in the past).

The scoring process is not used to select the "best" technology in each category. Rather the results are used as a guide for selecting technologies that could be grouped together to create an RAA. The RAAs developed after the technology scoring are described in Appendix A.

5.3 ANALYSIS OF DECISION ANALYSIS DATA AND CONCLUSIONS

This type of approach has many benefits, as described below:

- It is a transparent and deliberate process that includes clear goals, clear screening criteria, and a complete array of remedial technologies to consider.
- It is quantitative and it conveniently and credibly documents the decision-making process.
- It fosters communication and discussion, and promotes consensus and commitment among participants.
- It can help reveal factors that are driving and not driving the decision and areas of uncertainty that need to be explored further.
- It can help identify where differences between technologies are meaningful (e.g., a small change in score or weight can result in another technology scoring higher) or not meaningful (e.g., no change in weight can change the result in the score). This helps stakeholders focus on discussions that are meaningful to technology rankings and help to prevent unnecessary debate around subjects that will not change the outcome.

Due to the compressed nature of the decision analysis activities, some components of the analysis could not be optimized in real time, as described below:

- Some technologies were discussed in more detail than others. This may have led to a better understanding of these technologies, which could have resulted in different scoring approaches then those technologies that were less well understood. However, any changes in scoring would be expected to be minor and would not have resulted in selecting one technology over another for the purpose of RAA development (i.e., the team did not explicitly develop RAAs strictly based on scoring ranking and considered technologies of similar scores as approximately equal).
- Not all technologies included in the decision analysis evaluation have the same scope of applicability. Some were deemed major components of the remedy and others were considered ancillary to another remedy. This may have resulted in different scoring approaches by the scorers.
- The scoring range used to evaluate technologies may have been too restrictive. While most scorers used the 25, 50, and 75 liberally, few scorers used values of 0 and 100. This led to clustering of results and less differentiation of values than if a wider range had been used.
- A sensitivity analysis on decision analysis scoring weights was performed and is presented in Appendix C. The sensitivity analysis shows that those technologies that were included in RAAs (Appendix A) due to their technology ranking from the decision analysis process would still have been chosen given reasonable changes in scoring weights.
- Scorers in the decision analysis session have different backgrounds and experience with the technologies and with the 100-D Area. While some scorers were knowledgeable about a wide range of technologies and the specifics of the 100-D Area, other experts were more focused on a smaller group of technologies or aspect of the 100-D Area. Variations in confidence with which different scores were made may not have been captured in the results.

The meeting participants did agree that the decision analysis session was useful in developing and screening technologies, and the meeting served its purpose in identifying which technologies should be considered for inclusion in RAAs.

6.0 PRE-CONCEPTUAL DESIGN AND COSTS FOR EX SITU GROUNDWATER TREATMENT TECHNOLOGIES

The existing ex situ treatment systems for the 100-D Area (100-HR-3 and DR-5) do not appear to have the treatment capacity that will likely be needed to achieve the current or potential future RAOs. Nevertheless, the results of the technology screening and decision analysis presented in Section 5.0 demonstrate that one or more ex situ pump-and-treat systems will likely remain an important component of any future RAAs implemented at the 100-D Area (see Appendix A). Consequently, substantial upgrades of the existing systems or their replacement by a larger system are being considered. Consistent with the objectives of the 100-D Area RPO, this section presents the design criteria, pre-conceptual designs, and rough order-of-magnitude cost estimates for three ex situ treatment systems that could be implemented at the 100-D Area to facilitate the achievement of RAOs. The information presented in this section is intended to support the effort to select the pump-and-treat system design that is most appropriate for the 100-D Area. Cost factors used in the analysis are summarized in Appendix D, and cost breakdown tables are included in Appendix E. Extraction and infiltration system components were not addressed as part of this evaluation.

6.1 DESIGN CRITERIA

The pre-conceptual design and rough order-of-magnitude cost estimates presented here for the ex situ treatment systems are based upon the facility, hydraulic, and chemical design criteria described below. The pre-conceptual designs cover only processes within the battery limits of the treatment building with the exclusion of groundwater extraction wells and conveyance pipes to and from the building. These design criteria are preliminary and may be updated as the RAAs being evaluated for the RPO are developed in more detail. For example, groundwater modeling will be used to refine the conceptual designs of the RAAs. Required flow rates will be based on this modeling.

A. Facility criteria:

- The ex situ treatment system pre-conceptual design shall consist of processes and equipment within the limits of a central treatment building.
- The design shall not include extraction or injection wells, associated piping or other infrastructure, the treatment building, roads, utilities, electrical service, or sanitary facilities.
- Design shall include height and area requirements for equipment, maintenance, and storage within the treatment building.
- Groundwater from extraction wells will be delivered to the treatment building without intermediate storage or treatment.
- The pre-conceptual design shall include provisions for capture, collection, and temporary storage of all regulated waste streams, whether liquid or solid, hazardous or radioactive, for disposal by others.

- The system will be designed so there is no offsite shipment of waste, resin, or other byproducts that could possibly be radioactively contaminated. (The baseline case of offsite regeneration was retained for comparison purposes.)
- Final wastes should be acceptable for onsite disposal at the ERDF.
- Process equipment should be designed to require minimum labor support.
- The pre-conceptual design shall include major control loops in sufficient detail to illustrate process control strategy and major process and ancillary equipment.

B. Hydraulic criteria:

- The pre-conceptual design shall include all process unit operations required to treat a sustained flow of groundwater from the 100-D Area at a nominal maximum rate of 5,680 L/min (1,500 gpm).
- The treatment process shall have the capacity to operate continuously at any flow rate between the nominal maximum flow rate and 40% of the nominal maximum flow rate to accommodate variations in well pump operation.

C. Chemical criteria:

- The interim ROD requires that the groundwater treatment system be able to reduce the effluent chromium concentrations to the maximum extent practicable. Treated groundwater with hexavalent chromium concentrations >50 μg/L will not be discharged. The regulatory criteria further require that hexavalent chromium concentrations be lowered to <20 μg/L at compliance monitoring locations.
- The treatment system shall be capable of treating groundwater constituents as summarized in Table 6-1. In addition, the treated water shall have a neutral pH and be essentially particulate-free to avoid scaling or plugging of injection wells. Although listed as a contaminant of concern, tritium will not be removed by the treatment system; instead, treated water will be reinjected to allow natural radioactive decay during migration through the subsurface formation(s).

Table 6-1. 100-D Area Design Influent and Effluent Concentrations.

Constituent	Units	Design Average Influent Concentration	Proposed Effluent Concentration
Hexavalent chromium	μg/L	100 to 500[a]	≤ 5 (goal); ≤ 20 (average); 50 (maximum)
Nitrate – as nitrogen	mg/L	< 10	< 10

[a] Recent discovery of a zone with over 40,000 μg/L needs further evaluation in a subsequent feasibility study.

6.2 ION EXCHANGE WITH OFFSITE REGENERATION

An IX system with offsite regeneration of spent resin serves as the base case against which other technologies can be compared. Offsite regeneration is the approach used throughout the 100 Areas, with the exception of the DR-5 system where resin is regenerated onsite by a more aggressive process than is typically employed.

6.2.1 System Description

As shown in Figure 6-1, the base case IX system consists of six parallel trains with four IX vessels per train. The IX columns are operated in series, three vessels in operation as lead, lag and polish, respectively, while the fourth vessel is in standby following regeneration. Spent resin from the lead vessel is shipped to the Siemens facility in Roseville, Minnesota, for regeneration. The mass balance for IX with offsite regeneration is shown in Appendix E (Table E-1). The equipment list and equipment layout in the treatment building are given in Table E-2 and Figure 6-2, respectively. The overall area for the process building is approximately 1,105 m^2 (11,875 ft^2).

Influent groundwater storage and pH adjustment occur in a 60,566-L (16,000-gal) HDPE tank. Tank sizing was based on the existing IX system at the 100-HR-3 facility. A sulfuric acid injection system reduces the groundwater pH to 7.0 to prevent precipitation of calcium carbonate on piping and the IX columns. The sulfuric acid flow is automatically adjusted based on the pH measured in the treated water tank by means of a feedback control loop. Alternately, acid feed could be controlled by flow-paced, feed-forward logic, since the water contains significant alkalinity. Process feed pumps transfer water to the IX column trains at a maximum flow rate of 5,678 L/min (1,500 gpm), although the IX process can operate at reduced flow rates. The actual flow rate depends on the production rate of the extraction wells and the level of water in the feed tank. Automated flow control valves distribute the flow equally to each train.

The **IX columns** are skid-mounted, with four 2-m (6-ft)-diameter vessels per train. The flow rate through each train is 946 L/min (250 gpm) at full system capacity. The pressure drop across the resin bed in a single column is approximately 29 kilopascal (4.2 psid) under clean conditions. At any one time, at least three columns will be treating water in lead-lag-polish configuration, with the fourth in standby for resin replacement. The valves and piping arrangement will allow flow through the columns in any sequence. Purolite A-500, a Type 1, macroporous, strong-base anion-exchange resin currently used in the DR-5 system, is also used in the current design because of its superior loading capacity and macroreticular structure relative to other resins considered. As with all industry standard resins, Purolite A-500 can be regenerated at the Siemens facility. Purolite A-500 is significantly less expensive than Dowex 21K resin ($130/$ft^3$ [$4,590/$m^3$] versus $266/$ft^3$ [$9,394/$m^3$]). The IX vessels were sized for 3.783 m^3 (133.6 ft^3) of resin to maintain a throughput rate of 15 bed volumes per hour at full flow.

A **backwash and sluicing system** is used to remove resin for regeneration. When hexavalent chromium breakthrough occurs, the lead column is backwashed with treated water to remove fines from the resin. The backwash water is filtered prior to being pumped back to the feed tank to be reprocessed. Treated groundwater is also used to sluice spent resin into 1.1-m^3 (40-ft^3) totes. As in the current systems, the sluice water drains into the collection sump prior to being

pumped into the feed tank. The resin is analyzed for radionuclides prior to shipping the totes to the Siemens facility for regeneration.

An **automated, multi-port analyzer** monitors performance of the IX system to verify that effluent concentrations are below allowable limits. This monitoring system includes alarms and a control that automatically shuts off the IX system if hexavalent chromium concentrations in any of the trains exceed allowable values. The individual trains are also monitored for water flow rates and system pressure drops. Manual sampling and analysis are used to verify hexavalent chromium concentrations throughout the system and to confirm on-line analyzer results. Additional characterization is also performed for chloride, sulfate, nitrate, and uranium concentrations across IX vessels and trains, to evaluate chromatographic sequencing and optimize the process.

6.2.2 Capital and Operation and Maintenance Costs

Concept screening-level capital cost and O&M cost estimates were prepared for the IX system with offsite regeneration. Equipment used in these pre-conceptual designs was selected based on use in applications similar to these processes, with equipment capacity and sizing based on process calculations suitable for the respective applications. These estimates were based on vendor information, telephone quotes, information from previous projects, and similar sources, with application of escalation factors (*Marshall and Swift Equipment Cost Index – Chemical Engineering* [Marshall and Swift 2008]) and capacity scale-up factors ("Design Cost Factors for Scaling-Up Engineering Equipment" [Remer et al. 1990]). The balance of the estimate used factors for installation, instrumentation and controls, piping, electrical, yard improvements, service facilities, engineering and supervision, construction expenses, administration and miscellaneous (includes permitting), and contractor's overhead and profit from *Plant Design and Economics for Chemical Engineers* (Peters and Timmerhaus 2003), as modified in Appendix D. The method outlined for fluid processing plants in Peters and Timmerhaus (2003) was selected because it is commonly used for preliminary and study estimates of the type described in this document; the purpose of these cost estimates is for screening and comparing alternative ex situ technologies for treating hexavalent chromium in groundwater. The cost estimates should not be used for budgetary purposes or as an indication of the actual cost for a project.

The estimated capital cost for removing hexavalent chromium from groundwater by this system is $16.3 million. The estimated annual O&M cost is $6.7 million. Capital and O&M cost breakdown information is provided in Appendix E (Tables E-3 and E-4), respectively.

6.3 ION EXCHANGE WITH ONSITE REGENERATION

An IX system with onsite regeneration of spent resin addresses concerns about long-haul transport of resin. Onsite regeneration is the approach used at the DR-5 area (Section 3.2).

Figure 6-1. Ion-Exchange System with Offsite Regeneration.

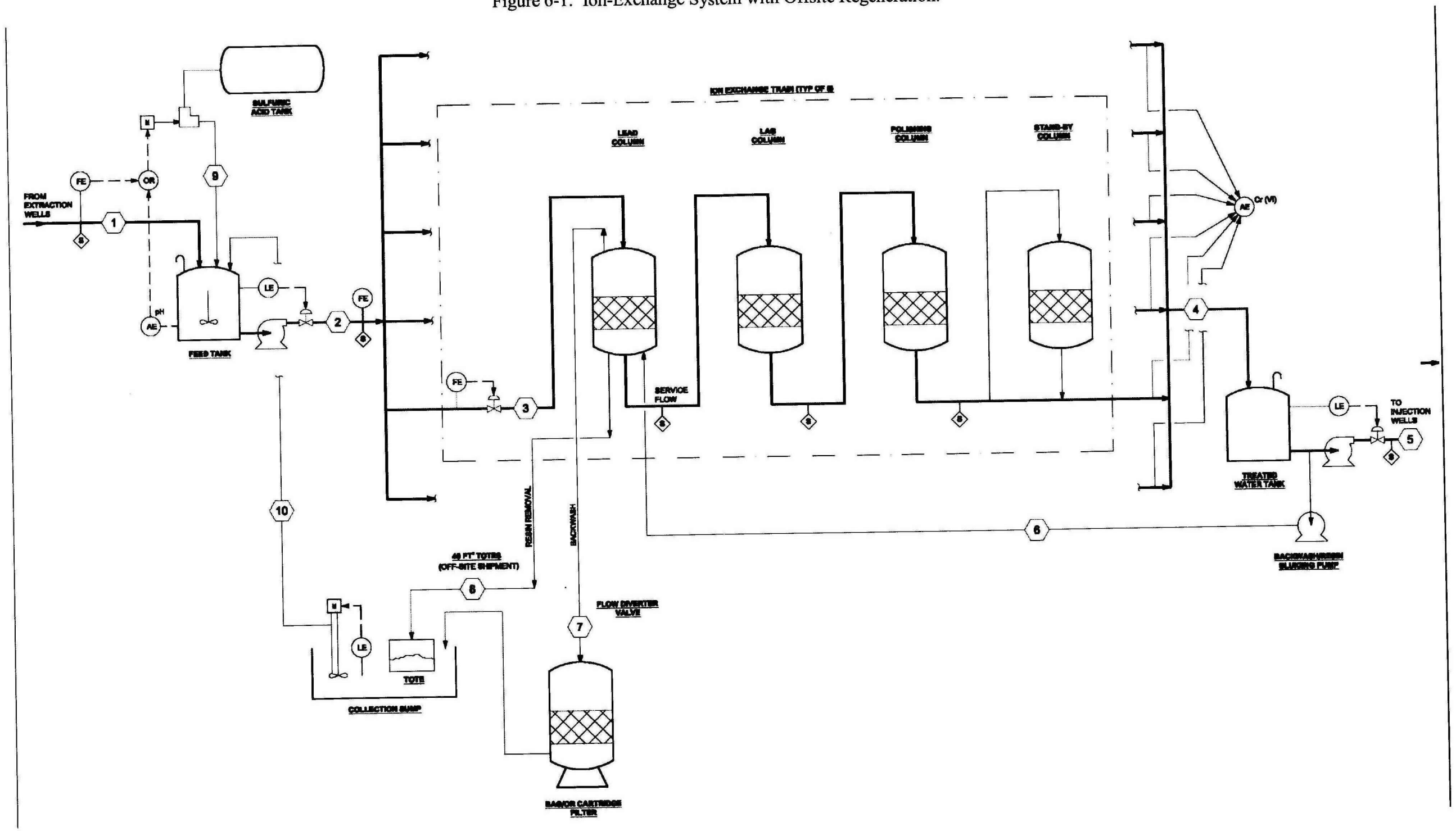
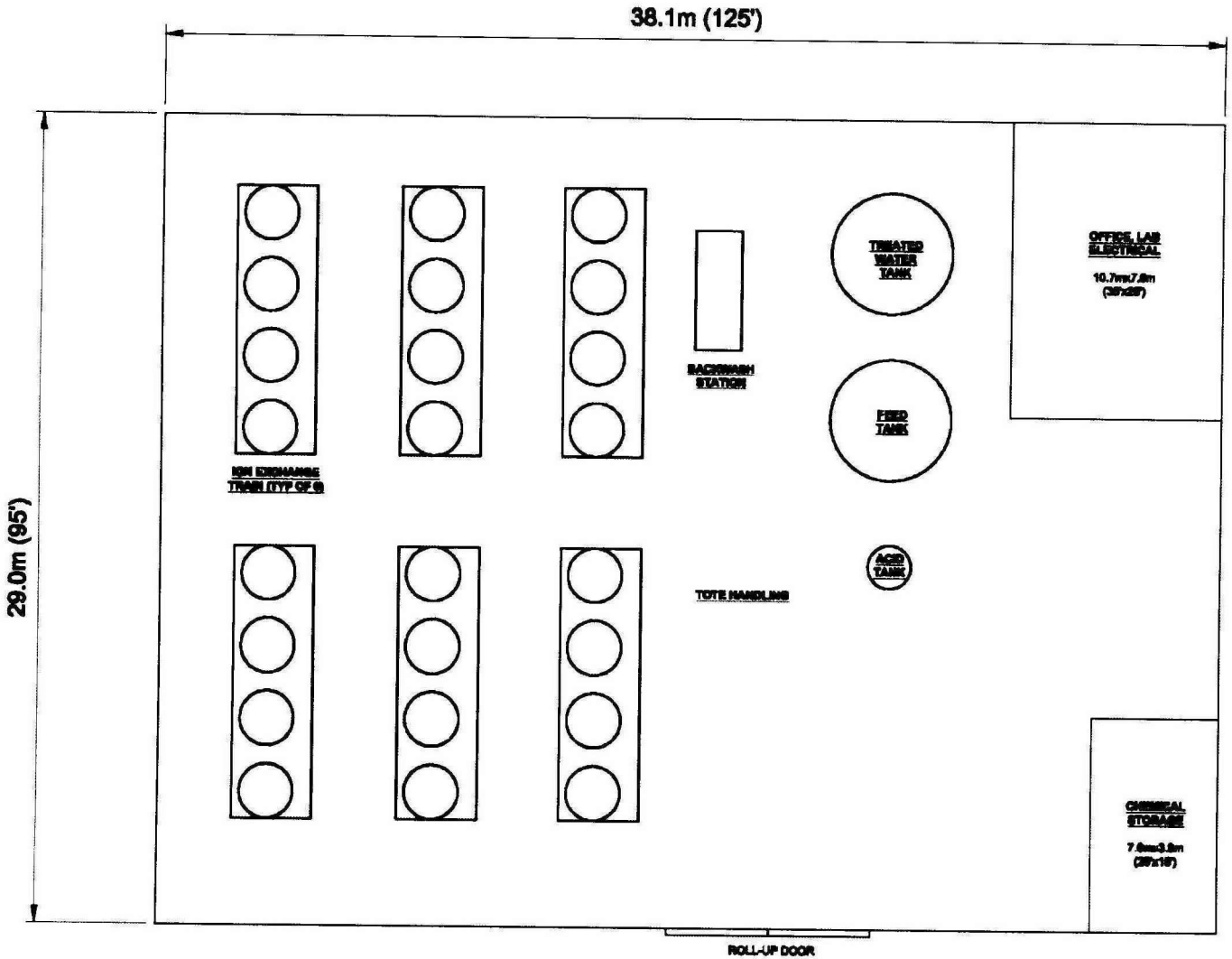


Figure 6-2. Building Layout for Ion Exchange with Offsite Regeneration.



6.3.1 System Description

While in service, the IX part of the process is identical to that of the above case for offsite regeneration, consisting of six parallel trains with four IX vessels per train. The IX columns are operated in series, three vessels in operation as lead, lag, and polish, while the fourth vessel is in standby mode following regeneration. The key difference is that spent resin is regenerated while still in the column, using a method different from that used for the DR-5 system. The overall process for IX with onsite regeneration is shown in Figure 6-3, with the mass balance appearing in Table E-5 of Appendix E. The equipment list and equipment layout in the treatment building are provided in Table E-6 and Figure 6-4, respectively. The overall area for the process building is approximately 1,363 m^2 (14,700 ft^2).

Influent groundwater storage and pH adjustment occur in a 60,566-L (16,000-gal) HDPE tank, identical in form and function to the case in which regeneration occurs offsite. Process feed pumps transfer water to the IX column trains at a maximum flow rate of 5,680 L/min (1,500 gpm), although the IX process can operate at reduced flow rates. The water is pumped and distributed as described previously for the IX system with offsite regeneration. Sulfuric acid reduces the groundwater pH to 7.0 to prevent precipitation of calcium carbonate on piping and IX columns.

The **IX columns** are skid-mounted, with four 2-m (6-ft)-diameter vessels per train and will operate exactly the same way described for the IX system with offsite regeneration. These columns will also use the same resin (Purolite A-500, a Type 1, macroporous, strong-base anion-exchange resin) and resin quantity (3.783 m^3 [133.6 ft^3]) as previously described. However, these columns will have slightly different internal configurations to provide for uniform distribution and collection of brine regenerant and slow rinses. Additionally, each column will include automatic valving and instrumentation for the regeneration cycle.

Backwashing removes fine resin fragments from the resin bed prior to actual regeneration, identical to the description for the IX system with offsite regeneration.

The process of IX regeneration is a three-step process. The first step consists of regenerating the resin by passing a 10% solution of sodium chloride brine, in an up-flow mode, through the bed at a low hydraulic rate. Up-flow regeneration efficiently removes hexavalent chromium from the resin at the bottom of the column to prevent leakage commonly encountered with co-current regeneration. The sodium chloride brine containing hexavalent chromium removed from the resin is diverted to the **regenerant treatment tank** for hexavalent chromium removal. The regenerant brine is prepared by saturating water with sodium chloride rock salt in the **salt saturator**. Saturated salt brine is periodically transferred to the **brine feed tank,** from which it is metered into a stream of treated water to produce 10% regenerant brine.

The second step consists of displacing the brine in the column with treated water, at the same low flow rate and volume as with the regenerant brine. This slow rinse stream also is sent to the regenerant treatment tank for hexavalent chromium removal.

Figure 6-3. Ion Exchange with Onsite Regeneration.

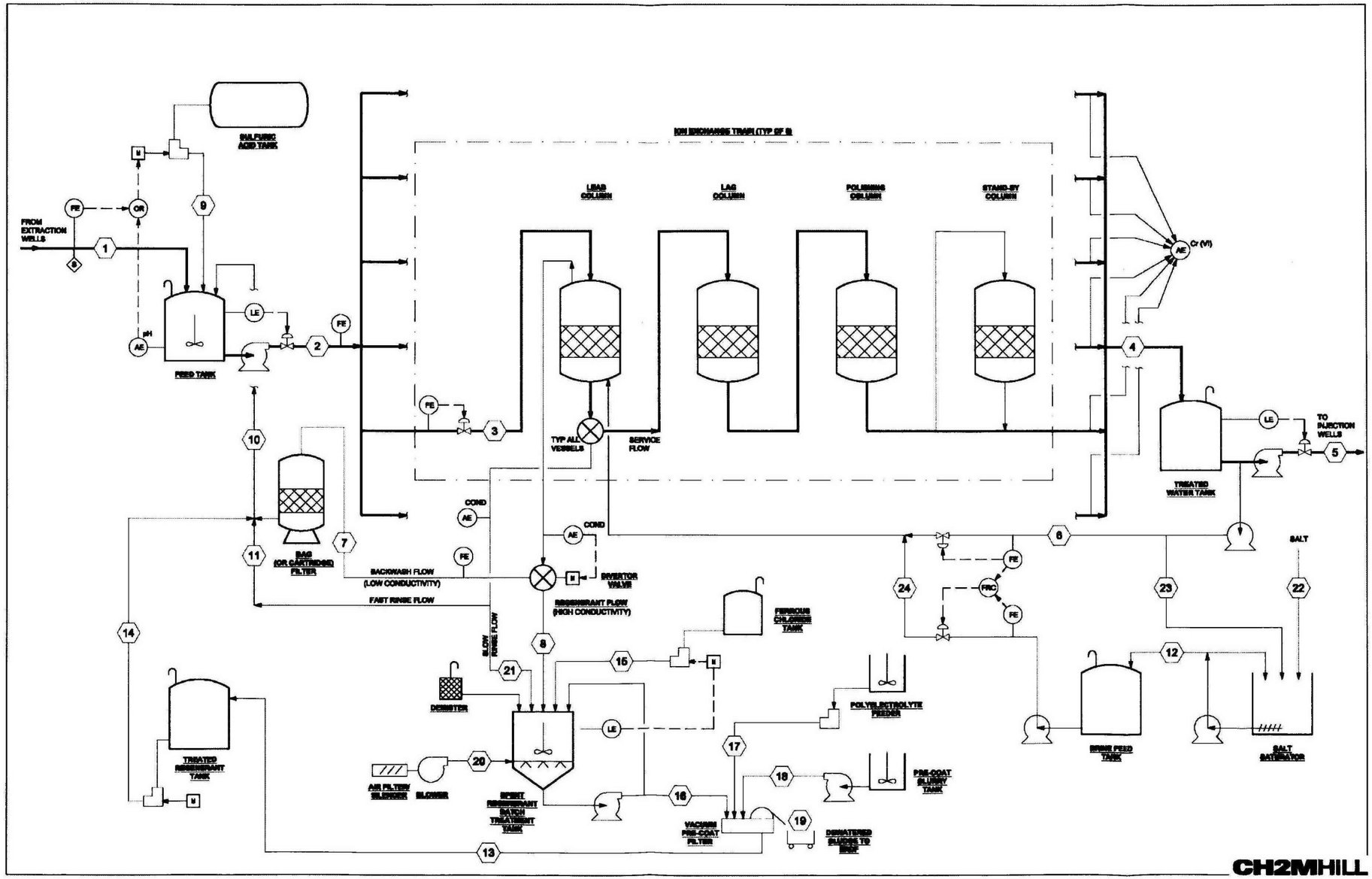
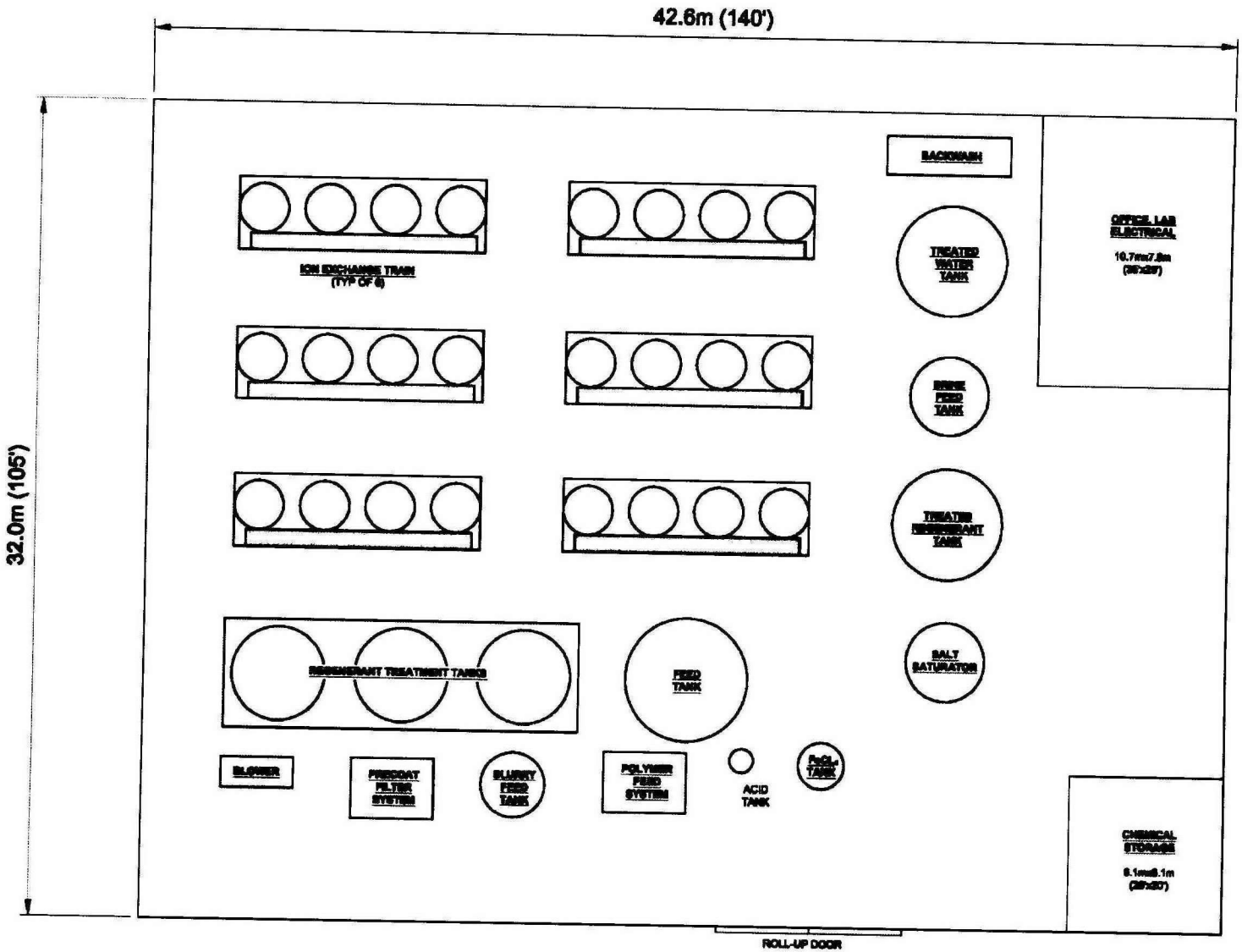


Figure 6-4. Building Layout for Ion Exchange with Onsite Regeneration.



The third step is a rinse with treated water at a higher flow rate and larger volume than the slow rinse. Fast rinse water is returned directly to the feed tank, to be reprocessed through the system.

Regenerant brine treatment involves addition of ferrous chloride to reduce hexavalent chromium to trivalent chromium, which precipitates from solution as a hydroxide. The ferrous iron that reacts with hexavalent chromium becomes oxidized to ferric iron and also precipitates as a hydroxide.

Residual ferrous iron remains after hexavalent chromium is reduced. The excess ferrous iron is oxidized by sparging air through the regenerant treatment tank to produce ferric iron, which precipitates as a hydroxide. Uranium removed from the IX resin during regeneration co-precipitates with the ferric hydroxide.

Solids formed when spent brine regenerant and slow rinse water are treated are filtered through a **vacuum pre-coat filter** to remove solids. The resultant solids-free stream is stored in the treated regenerant tank and slowly metered back to the feed tank to be reprocessed through the IX system. Process calculations indicate that the secondary MCL for chloride would not be exceeded by controlled flow of brine to the feed tank. Protection against injection well plugging is provided by oxidation of ferrous iron to form insoluble ferric hydroxide and treated water filtration through an ultrafine pore-size microfilter. Confirmatory testing and evaluation are advised to verify overall feasibility of this approach to treated regenerant management.

6.3.2 Capital and Operation and Maintenance Costs

Concept screening-level capital and O&M cost estimates were prepared as described in the previous section and again should not be used for budgetary purposes or as an indication of the actual cost for a project.

The estimated capital cost is $14.7 million. The estimated annual O&M cost is $2.3 million. Capital and O&M cost breakdown information is provided in Appendix E (Tables E-7 and E-8, respectively).

6.3.3 Areas for Further Evaluation

Onsite treatment of sodium chloride-based regenerant brines is an uncommon practice, and the approach presented in this process description should be verified experimentally before implementation is considered. The principles used in the pre-conceptual approach to onsite IX regeneration and treatment of regenerant brine are based on familiar practices used in different applications.

The feasibility of reintroducing treated regenerant brine to the feed tank also needs experimental verification. The chromatographic sequencing of constituents in IX column effluent is currently unknown, so it is not certain whether nitrate will accumulate in treated brine and compete with hexavalent chromium for resin binding sites. It is also not known to what extent chloride released from the IX resin will contribute to chloride concentrations in treated water, nor whether the chloride concentrations will approach or exceed the secondary MCL.

6.4 FERROUS CHLORIDE PROCESS

Ferrous chloride and ferrous sulfate have been used to reduce hexavalent chromium for over 70 years and have found use in industry as well as groundwater treatment.

6.4.1 System Description

Ferrous chloride was chosen as the hexavalent chromium reducing agent because it has been evaluated by the City of Glendale, California ("Hexavalent Chromium Removal by Reduction with Ferrous Sulfate, Coagulation, and Filtration: A Pilot-Scale Study" [Qin et al. 2005]). The ferrous chloride treatment process is shown schematically in Figure 6-5 and is summarized below. Stream numbers given in the process flow diagram are identified and materials quantities are provided in the mass balance in Appendix E, Table E-9. Process equipment was sized according to intended function and each item is identified in the equipment list, Table E-10, as well as capacities and approximate dimensions. Figure 6-6 is a layout drawing showing approximate placement inside the treatment building. The overall area for the process building is approximately 1,414 m^2 (15,225 ft^2).

Hexavalent chromium reduction is performed by adding an excess of ferrous chloride to hexavalent chromium-contaminated groundwater in a stirred-tank reactor with a hydraulic residence time of 5 minutes. The hexavalent chromium is reduced to the trivalent state by the ferrous iron. A second reactor in series with the first allows the hexavalent chromium reduction reaction to continue without interference from high hexavalent chromium feed water entering the first reactor. The reaction is carried out at a pH of 6.0 to prevent dissolved oxygen from competing with hexavalent chromium for the available ferrous iron ("Removal of Chromium[VI] from Drinking Water by Redox-Assisted Coagulation with Iron[II]" [Lee and Hering 2003]). The reaction rate used in sizing the reactors was based on pseudo-first order kinetics, approximated from a more complex relationship ("Kinetics of Chromate Reduction by Ferrous Iron" [Fendorf and Li 1996]).

Ferrous iron oxidation is carried out to prevent iron fouling of groundwater injection wells after the water has been treated. The pH is increased to at least 7.0 to 7.5, and air is sparged into three oxidation reactors in series to reduce residual iron to below 10 to 25 μg/L. The oxidation rate of ferrous iron is constrained by limits to the pH of water that can be reinjected without causing calcium carbonate to foul the injection wells using a published kinetic equation ("Kinetics and Product of Ferrous Iron Oxidation in Aqueous Systems" [Sung and Morgan 1980]). Each oxidation reactor has a hydraulic residence time of 30 minutes to reduce residual ferrous iron to the target effluent concentration from the third reactor.

Clarification significantly reduces the concentration of solids precipitated during hexavalent chromium reduction and ferrous iron oxidation. Gravity settling is enhanced through use of a synthetic, usually acrylate-based, polyelectrolyte, which agglomerates iron hydroxide floc particles into larger, faster-settling particles. A very high fraction of the suspended solids entering the clarifier are recycled back to the first oxidation reactor to provide nucleation sites for newly-precipitated solids. Sludge is wasted at the same rate at which it forms in the process. Water in the clarifier overflow stream contains as much as 25 mg/L of suspended solids, which is too high a concentration for direct injection.

Microfiltration removes ferric iron floc particles from the clarifier overflow stream by filtration through a microfilter with 0.1 micron pores. The microfilter is automatically backwashed at predetermined intervals (typically hourly), with solids enriched backwash water captured in a **dirty backwash tank** and then reprocessed through the treatment plant. Precipitated solids are purged from the system through the clarifier underflow stream.

Treated water is stored in the **treated water tank** from which it is pumped to injection wells. The hexavalent chromium concentration in treated water will be below the 20 μg/L limit for groundwater, and probably significantly below 5 μg/L. The ferrous chloride process would also reduce the naturally occurring uranium concentration to below 1 μg/L through co-precipitation with the hydrous iron floc. Nitrate and sulfate concentrations are unchanged by the ferrous chloride process. Treated water is expected to meet secondary MCLs for chloride and sulfate, and should not exceed the secondary MCL of 10 mg/L for nitrate as nitrogen.

Process sludge is wasted to the **sludge holding tank** for temporary storage. Periodically the sludge is pumped from the tank for dewatering. Sludge from the sludge holding tank is dewatered with a **vacuum pre-coat filter**. The pre-coat filter is initially coated with a 7.6- to 15.2-cm (3- to 6-in.) layer of diatomaceous earth, which is held in place by the vacuum maintained inside the fabric-covered drum. The pre-coated drum rotates slowly, continuously exposing a fresh pre-coated surface through which liquid is pulled, leaving precipitated solids on the pre-coat layer. A small amount of synthetic polyelectrolyte is added to the sludge to improve its dewatering characteristics. After sludge solids have loaded onto the pre-coat layer and water has passed into the interior of the drum, the drum rotates further, and on the downward stroke, encounters a "doctor" blade that shaves off a small amount of the pre-coat, along with process solids. The water that passes though the pre-coat layer into the drum is collected in a vacuum system sump and is pumped back to the front of the process.

6.4.1 Capital and Operation and Maintenance Costs

Concept screening-level capital and O&M costs were prepared as described previously and again should not be used for budgetary purposes or as an indication of the actual cost for a project.

The estimated capital cost is $15.6 million. The estimated annual O&M cost is $2.9 million. Capital and O&M cost breakdown information is provided in Tables E-11 and E-12 of Appendix E.

6.4.2 Areas for Further Evaluation

As with most new applications of established technology, experimental verification is needed to confirm that the approach is robust. Although successfully applied for treating hexavalent chromium in brackish groundwater, investigations have shown that in low ionic strength solutions, atmospheric oxygen competes with hexavalent chromium for the added ferrous iron (Lee and Hering 2003).

Figure 6-5. Ferrous Chloride Treatment System.

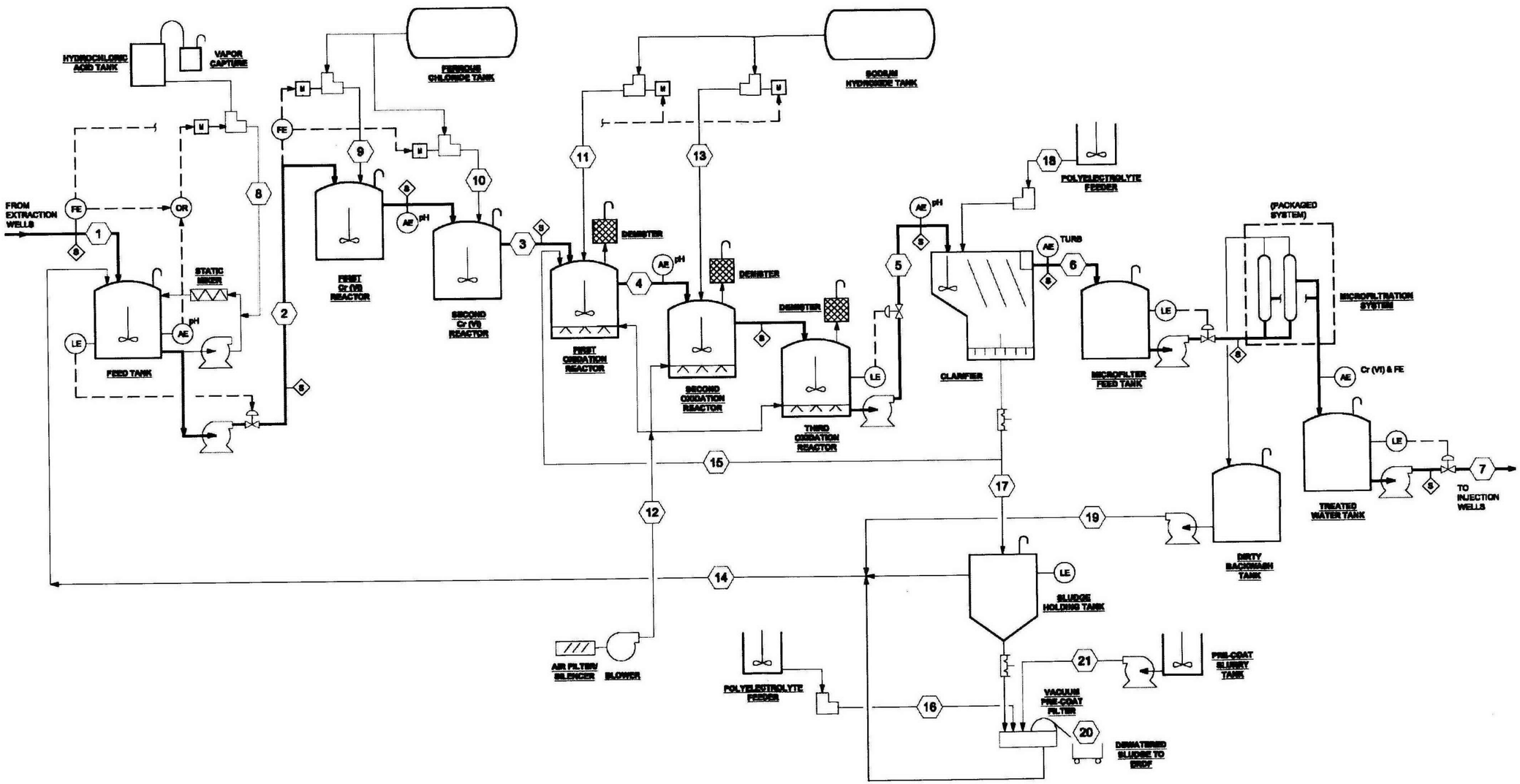
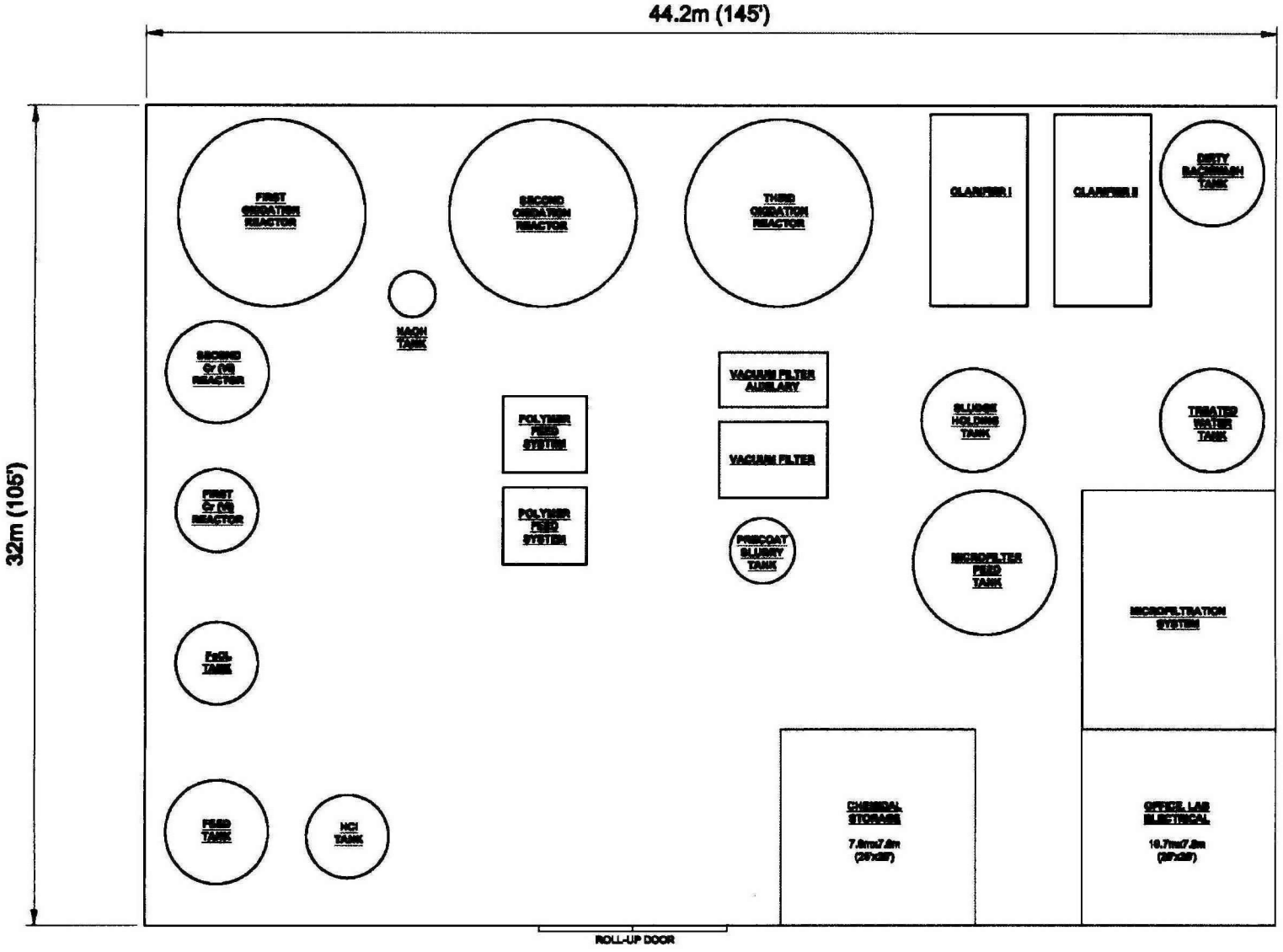


Figure 6-6. Building Layout for Ferrous Chloride Treatment System.



6.5 TECHNOLOGY COMPARISON

Removal of hexavalent chromium in groundwater by IX with offsite regeneration is currently in use in the 100-HR-3 facility. This technology was included in the evaluation as a base case against which the other technologies could be compared, with the exception that another type of strong-base, anion-exchange resin with a higher loading capacity was assumed in place of the resin currently used in the 100-HR-3 system. The other two technologies were selected because hexavalent chromium would likely be removed as efficiently as with the existing 100-HR-3 system, and each offered some potential advantages not available with the case involving offsite regeneration.

The IX with onsite regeneration of spent resin was included after an initial evaluation indicated that secondary MCLs for chloride and sulfate would not be exceeded if regenerant brine were treated to remove hexavalent chromium and the treated brine was co-injected with treated groundwater into the aquifer. The ferrous chloride process was included because it is capable of meeting the RAO for hexavalent chromium in groundwater and does not produce a waste brine stream.

The three technologies are compared for several important characteristics in Table 6-2. It is noteworthy that the significantly higher O&M cost for IX with offsite resin regeneration comes from resin shipping and regeneration (50% of total O&M) and from radiological analysis of the resin (24%). The system with the lowest O&M cost was IX with onsite regeneration. Although the same ferrous chloride-based process would be used to treat the relatively small regenerant brine volume in the onsite IX regeneration and total extracted groundwater stream (when IX is not used), the cost for treatment chemicals and waste disposal is lower for regenerant brine treatment than for treating the entire groundwater stream. Both of these ferrous chloride-based processes would have lower costs than when spent IX resin is regenerated offsite.

Mass balances for each of the technologies (Appendix E, Tables E-1, E-5, and E-9) show that MCLs for chloride and sulfate will not be exceeded, even with co-injection of brine with treated water into the aquifer. However, nitrate is eluted along with hexavalent chromium during regeneration and could potentially exhaust the resin prematurely if the treated regenerant is returned to the feed tank. If that possibility is confirmed, the treated brine could be co-injected with treated water to avoid nitrate build-up in the IX regenerant brine circuit.

The existing IX system at 100-HR-3 with offsite regeneration produces a solid waste during the backwash cycle. This waste stream consists mainly of small, broken IX beads, which are produced at an approximate rate of 6,300 kg/year (7 tons/year). The annual waste rate from the onsite regeneration system would be 102,000 kg/year (112 tons/year), including the broken resin particles along with sludge and diatomaceous earth filter aid from the hexavalent chromium removal system for treating the waste brine stream prior to co-injection with treated water into the aquifer. The ferrous chloride process produces the largest waste stream, 392,000 kg/year (432 tons/year), consisting of iron hydroxide, chromium hydroxide, and diatomaceous earth filter aid. None of these waste streams contain free water by the EPA paint filter test, and all should pass TCLP testing as nonhazardous wastes. Characterization for disposal on land is needed.

Table 6-2. Ex Situ Hexavalent Chromium Treatment Technology Comparison.

	Ion Exchange with Offsite Regeneration	**Ion Exchange with Onsite Regeneration**	**Ferrous Chloride**
Expect to meet overall RAOs	Yes	Yes	Yes
Expect to meet secondary MCL for chloride	Yes	Yes	Yes
Expect to meet secondary MCL for sulfate	Yes	Yes	Yes
Ability to operate continuously at reduced flow rate	Yes	Yes	Yes
Regenerant brine management	N/A	Meter back to feed tank or co-dispose with treated water	N/A
Solid waste quantity 1,000 kg/year (tons/year)	6.3 (7)	102 (112)	392 (432)
Expect to pass TCLP test	Yes	Yes	Yes
Estimated capital cost ($ million)	16.3	14.7	15.6
Estimated annual O&M cost ($ million)	6.7	2.3	2.9

N/A = not applicable
MCL = maximum contaminant level
O&M = operation and maintenance
TCLP = toxicity characteristic leaching procedure
RAO = remedial action objective

6.6 CONCLUSIONS AND RECOMMENDATIONS

Each of the three technologies will remove hexavalent chromium from groundwater in the 100-D Area, and all three should meet required treated water quality criteria. The capital costs of all three technologies were very similar, despite differences among the processes. The O&M costs were the most significant differentiator. The technology with the lowest estimated O&M cost is IX with onsite regeneration; the estimated O&M cost for the ferrous chloride process was approximately 20% higher. The largest solid waste stream is generated by the ferrous chloride process, and smallest stream is generated by IX with offsite regeneration.

The process of IX with onsite regeneration uses the least well-established approach to manage spent sodium chloride regenerant brine and poses some technical risk that may be addressed by testing and evaluation. The ferrous chloride process is a known technology that is less technically challenging relative to IX with onsite regeneration.

The following recommendations are oriented toward verifying performance and reducing potential risks associated with onsite regeneration. The optimum operating conditions of the ferrous chloride process should also be evaluated.

- The chromatographic sequence of anionic constituents in 100-D Area groundwater should be determined to establish whether the concept of returning treated regenerant brine to the feed tank is necessary or if co-disposal with treated groundwater would be acceptable.
- The reaction rates of ferrous iron with hexavalent chromium and dissolved oxygen should be investigated as a function of pH to optimize use of treatment chemicals in treating the spent regenerant brine prior to disposal.
- Similar testing should be performed for the ferrous chloride process to establish the optimum pH and ferrous chloride dosage needed to reduce the hexavalent chromium concentration to the lowest practical level.
- Non-regenerable IX resin should be investigated for potential future use at the 100-D Area to confirm preliminary favorable economics, more fully evaluate technical feasibility, assess material handling attributes, and determine acceptability for disposal at the ERDF.

7.0 CONCLUSIONS AND RECOMMENDATIONS

The 100-D Area has a number of ongoing groundwater issues that have received, and will continue to receive, focused attention from the DOE and stakeholders. The RPO efforts have been undertaken at the 100-D Area to assist with addressing some of these issues . In particular, the RPO efforts have focused on addressing protection of the river and achieving plume cleanup. They have also looked at reducing the cost and improving the performance of the existing systems.

This technical memorandum reports on five of the seven RPO tasks, as follows:

- Reviewed and summarized the CSM and discussed implications for site remediation
- Reviewed the design and performance of the existing 100-D Area ex situ remedial systems and treatability actions; identified system or process modifications to improve performance
- Identified and screened in situ and ex situ remedial technologies with the potential to improve remedial performance at the site
- Developed and summarized potential RAAs for the site based on the screened technologies
- Developed pre-conceptual designs and costs for three pump-and-treat technologies that were identified during the screening process as candidates for inclusion into one or more of the proposed RAAs.

The two remaining RPO tasks will be completed after this document has been accepted by RL and will be documented in subsequent documents within the first quarter of FY09. The remaining tasks to be completed are as follows:

- Develop pre-conceptual level designs and costs for the RAAs and screen the RAAs using appropriate decision analysis tools that incorporate the CERCLA criteria for evaluation. A decision analysis workshop will be held to screen the RAAs. These results will be included in a final document that will describe the overall remedial approach that is recommended for the 100-D Area.
- Develop a process and control optimization plan for the iterative and continuing optimization of the existing and potential future 100-D Area pump-and-treat systems.
- Perform pilot testing of some of the components of the preferred alternatives may be necessary. It is currently envisioned that any pilot testing would be implemented as soon as possible in order to enable full-scale implementation of some of the components in FY09/FY10.

These activities will also be closely integrated with other ongoing activities:

- Actions that will address the hot spot areas (e.g., near the old sodium dichromate transfer station and other areas where sodium dichromate product was handled). The objective of these actions will be to remove a significant portion of the contaminant mass from the vadose zone hot spot(s) contributing to the groundwater plume(s). These actions can be considered near-term actions and are likely to be implemented in FY09/FY10.
- The RI/FS process. Currently, an integrated RI work plan is being developed for 100-D Area RI/FS activities. This process will lead to a final ROD for the site.

7.1 REVIEW CONCEPTUAL SITE MODEL

The following conclusions emerged during the review of the CSM, as it is currently understood:

- Simplistically, the site geology is composed of very coarse sands and gravel (including cobbles), but there are also some stringers of silts and sands.
- The average depth of groundwater is 21 m (70 ft) bgs; thus, the vadose zone is relatively thick.
- The Columbia River stage has a significant impact on groundwater levels and flow paths. During parts of the year, the river stage is higher than adjacent groundwater elevations.
- Widespread discharge and leaks of cooling water containing about 2 mg/L of hexavalent chromium, and mounding of groundwater during operations, resulted in a widespread hexavalent chromium plume at or below this concentration.
- More localized releases of concentrated chromate solutions resulted in higher concentration hot spots in some of the areas where these more concentrated solutions were historically handled or transported. Hot spots include high concentrations of hexavalent chromium in porewater in the vadose zone. These hot spots in the vadose zone and saturated zone likely serve as continued sources of contamination to the groundwater plume. Not all of these hot spots have been identified, and it may be very challenging to ever identify them all.
- The hexavalent chromium plume is divided into a northern plume and a southern plume as a result of leaks from the 182-D reservoir. Concentrations as high as 40,000 μg/L have been measured in one of the hot spots.
- Groundwater with hexavalent chromium concentrations >20 μg/L currently exists in monitoring wells close to the river and likely discharges to the river during part of the year at concentrations >20 μg/L.
- These concentrations exist despite the interim remediation systems that have been in operations for over 10 years. Although the interim remediation systems were not designed to address the entire plume, the persistence of the plume may support the conclusion that there are ongoing primary and/or secondary sources of hexavalent chromium contamination. Enhanced, modified, or supplemental remedial actions may be necessary to address the above issues.

7.2 REVIEW OF CURRENT EX SITU TREATMENT SYSTEMS AND OPTIMIZATION STUDIES

The design and operational processes of the 100-HR-3 and the DR-5 treatment systems were reviewed ,and actions to optimize the performance and reduce operational costs were identified. The results of an electrocoagulation pilot test study were also evaluated in order to determine whether this technology should be considered as an alternative to IX as an ex situ treatment technology at the 100-D Area.

7.2.1 100-HR-3 System

The 100-HR-3 system has been in operation since 1997, treating groundwater from the 100-D and 100-H Areas. In recent years, total availability has exceeded 95%, hexavalent chromium removal efficiencies are approximately 95%, and effluent hexavalent chromium concentrations are generally <20 μg/L. However, the actual capacity of the resin is approximately 1.5% of the manufacturer's stated total loading capacity. FH is constructing a test bed to evaluate a number of IX resins under various operating parameters in an effort to extend resin life and reduce O&M costs. A number of detailed recommendations for potential operational improvements and optimization of the 100-HR-3 IX facility were developed and are presented in Section 6.2.

7.2.2 DR-5 System

The DR-5 IX system was initially installed in the 100-D Area in 2004 to treat contaminated groundwater from the southern part of the northern plume that was not captured by the 100-HR-3 pump-and-treat system. The DR-5 system differs from other systems in the 100 Areas in that the IX resins are regenerated within the system rather than being shipped offsite for regeneration.

The system has met all design goals with the exception of unattended operation of the regeneration system. The resin has not been replaced since the system was installed. FH has initiated optimization of the regeneration and precipitation processes to reduce O&M costs and reduce generated quantities of solid waste and wastewater. Additional detailed recommendations are provided in Section 6.3.

7.2.3 Electrocoagulation Treatability Investigation

Electrocoagulation has been proposed as a potential alternative to the existing IX process for removing hexavalent chromium from groundwater in the 100-D Area. Electrocoagulation was believed to offer several advantages over IX, including reduced cost and increased operational simplicity. Another point of interest for electrocoagulation is that it does not increase the dissolved solids concentration of the treated water, as occurs with more conventional chemical precipitation processes. Pilot testing was carried out at the 100-D Area for the purpose of determining the effectiveness of hexavalent chromium removal and verifying the robustness, implementability, and scalability to larger size of the electrocoagulation process.

Electrocoagulation was able to reduce hexavalent chromium concentrations to <20 μg/L, but only when electrodes were clean. The initial current efficiency was approximately 1.8% at 60 amps, but after electrode passivation progressed, the current efficiency fell to 0.18% as the current increased to 600 amps. Operation of the system at high current density was ineffective for "burning" the passive layer off the electrodes. In addition, anode cleaning with hydrochloric

acid was ineffective and did not restore cell performance. Labor-intensive mechanical cleaning was required.

Solid wastes produced passed toxicity and corrosivity criteria and, with modifications to the system unrelated to the electrocoagulation process, this waste should also pass the "paint filter" test. The electrocoagulation unit was unable to operate unattended, failing to meet a key operational objective. The estimated cost to treat groundwater during the test was approximately 10 to 20 times the cost of IX treatment at the 100-D Area. The data obtained during pilot testing were not sufficient for scale-up to larger hydraulic capacity without further engineering assessment. A number of detailed recommendations are provided in Section 6.4 if electrocoagulation is to be pursued further.

7.3 TECHNOLOGY EXCHANGE MEETING

A hexavalent chromium treatment technology exchange meeting was initiated so RL and FH staff could obtain information regarding full-scale remediation of hexavalent chromium-contaminated groundwater. The presenters and meeting attendees generally agreed that the optimization of the current pump-and-treat systems and/or incorporation of new IX media or treatment technologies may provide cost and performance benefits. However, there was also a general consensus that treatment of the hexavalent chromium plume in the 100-D Area with the ISRM treatment zone and pump-and-treat technology alone would require long periods of time to achieve RAOs.

To accelerate remediation, a more aggressive approach that potentially uses both ex situ and in situ technologies to address both the groundwater and the vadose zone was recommended. There was particular interest in the in situ reduction of hexavalent chromium that can be accomplished using either chemical or biological approaches, or a combination thereof. Whichever approach or combination of approaches is ultimately implemented, it was recognized that it will be important to achieve and maintain hydraulic control of in situ treatment areas to ensure protection of the Columbia River and to avoid potential impacts (e.g., bio-fouling) to the pump-and-treat systems that are currently in place.

7.4 TECHNOLOGY SCREENING AND DECISION ANALYSIS

A technology screening meeting was held to identify new or alternative remedial technologies with the potential to accelerate remediation and closure of the 100-D Area. In addition to presentations about several key technologies, the meeting involved (1) identifying working RAOs that are likely to be formalized in the final ROD for the 100-D Area, (2) formulating technology screening criteria that would be used to rank the technologies, (3) brainstorming to create a list of potential technologies, (4) screening the potential technologies against the agreed-upon screening criteria, and (5) combining high scoring technologies into RAAs that could potentially achieve RAOs and that should be evaluated for the 100-D Area. A total of 10 final technology screening criteria were used that related to effectiveness, implementability, and cost. A total of 45 technologies were screened that fell into the following categories: (1) river protection, (2) vadose zone remediation, (3) groundwater remediation, and (4) ex situ groundwater treatment. The results of screening the individual technologies are as follows:

- Biological technologies tended to be highly scored, followed closely by chemical technology counterparts.
- The top-scoring river protection technologies were: biological barrier, followed by hydraulic barrier using injection at river, sparging wells, and chemical barrier.
- Top-scoring vadose zone treatment technologies were: biological infiltration, followed by chemical infiltration, remove/treat/dispose, and water flushing.
- Top-scoring groundwater treatment technologies were: in situ biological treatment, followed by in situ chemical treatment, in situ biological barrier, and in situ chemical barrier.
- Top-scoring ex situ groundwater treatment technologies were: optimize existing systems, followed by re-infiltration with biological amendments, ferrous iron reduction, and continue all actions (keep using IX as in the past).

Eight RAAs were developed by combining favored technologies from among the four categories above. These RAAs and will be evaluated in a subsequent task.

7.5 PRE-CONCEPTUAL DESIGN AND COSTS FOR EX SITU GROUNDWATER TREATMENT

The DOE is considering upgrading or replacing the existing ex situ treatment systems for the 100-D Area as part of the ongoing RPO effort. This section presents design criteria, pre-conceptual designs, and rough order-of-magnitude cost estimates for three ex situ treatment approaches that may be able to treat groundwater more cost-effectively than the current systems at the 100-D Area. The three approaches are (1) IX with offsite regeneration, (2) IX with onsite regeneration, and (3) the ferrous chloride process.

All three technologies will remove hexavalent chromium from groundwater and meet water quality criteria for the treated water. The estimated capital costs of all three technologies were very similar, despite differences among the processes. Estimated O&M cost was the most significant differentiator. The technology with the lowest estimated O&M cost is IX with onsite regeneration, followed by the ferrous chloride process estimated O&M costs that are approximately 20% higher. The largest solid waste stream is generated by the ferrous chloride process, and the smallest solid waste stream is generated by offsite regeneration.

The process of IX with onsite regeneration uses the least well-established approach to managing spent regenerant brine, and poses some technical risk that may be addressed by testing and evaluation. The ferrous chloride process is a technology that is less technically challenging relative to IX with onsite regeneration.

The following recommendations are oriented toward verifying performance and reducing potential risks associated with onsite regeneration. The optimum operating conditions of the ferrous chloride process should also be evaluated.

- The chromatographic sequence of anionic constituents in 100-D Area groundwater should be determined to establish whether the concept of returning treated regenerant brine to the feed tank is necessary or if co-disposal with treated groundwater would be acceptable.
- The reaction rates of ferrous iron with hexavalent chromium and dissolved oxygen should be investigated as a function of pH to optimize use of treatment chemicals in treating the spent regenerant brine prior to disposal.
- Similar testing should be performed for the ferrous chloride process to establish the optimum pH and ferrous chloride dosage needed to reduce the hexavalent chromium concentration to the lowest practical level.
- Non-regenerable IX resin should be investigated for potential future use at Hanford to confirm preliminary favorable economics, more fully evaluate technical feasibility, assess material handling attributes, and determine acceptability for disposal at the ERDF.

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APPENDIX A

PROPOSED REMEDIAL ALTERNATIVES

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APPENDIX A
PROPOSED REMEDIAL ALTERNATIVEAS

This appendix provides brief descriptions of the remedial action alternatives (RAAs) that were developed during the technology screening and decision analysis meeting. These RAAs were developed by combining the most highly rated technologies from the decision analysis session. The components of the RAAs are summarized in terms of the components that address the working remedial action objectives (RAOs). They will be developed in more detail and feasibility study-level designs and cost estimates will be prepared over the next few months.

A1.0 ALTERNATIVE 1 – ALL BIOLOGICAL TREATMENT

1a: More wells (thus, faster).

1b: Moderate number of wells.

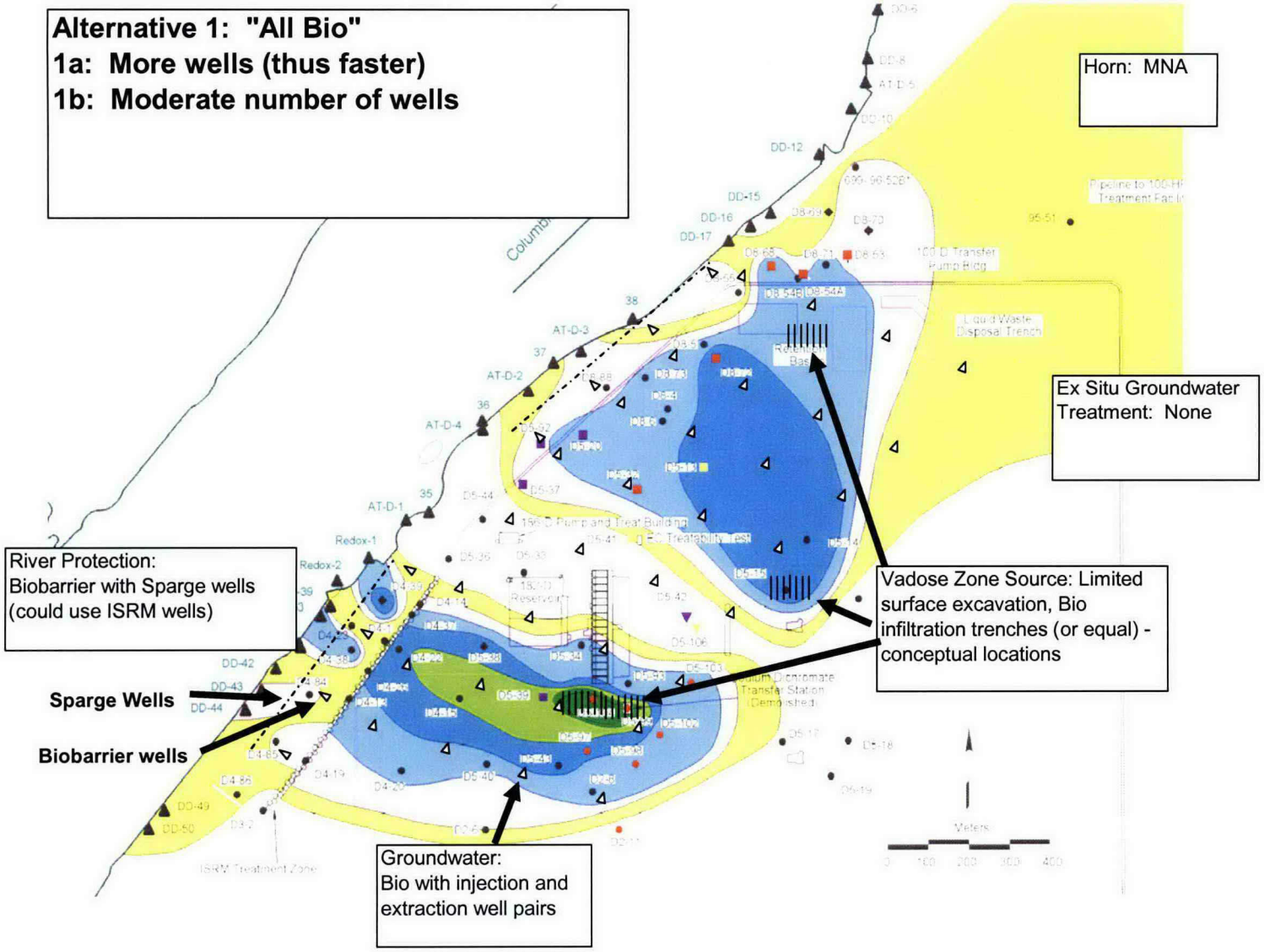
Summary:

This alternative uses biological treatment to aggressively achieve the RAOs for all media. It includes infiltration of biological substrate (i.e., carbon source) for the vadose zone source areas, in situ biological treatment via injection and extraction of biological substrate for the groundwater, and a biological reduction zone coupled with air sparging to protect the river. The same approach is used for the northern and southern plumes. Figure A-1 illustrates the components.

Components:

- Vadose zone source areas: Bioremediation via infiltration of an organic substrate as well as limited excavation would be used to treat the known vadose sources of hexavalent chromium. The excavations currently ongoing as part of the River Corridor Contract program would continue. The extent and depth of these excavations is currently being evaluated. At a minimum, some shallow soil excavations would take place. Bioremediation would be used for other shallow areas and for deeper source areas. Excavated soil would be disposed at the Environmental Restoration Disposal Facility (ERDF). Since not all these sources can be accurately located, the infiltration would be carried out over a larger area to be conservative. The infiltrated organic substrate would reduce the hexavalent chromium to its reduced form, causing it to precipitate on and be filtered out by the vadose zone soils. The infiltration would be performed using a drip irrigation type of system or infiltration trenches. Untreated extracted groundwater (amended with organic substrate) would be used as the source of infiltrate water. The carbon source could be an alcohol (e.g., ethanol), an organic acid (e.g., lactate), or a sugar (e.g., high fructose corn syrup). Locally available carbon sources such as winery byproducts or apple processing byproducts could also be considered.

Figure A-1. Alternative 1.



- Groundwater plume: The plumes would be treated using injection-extraction paired wells that would inject groundwater amended with the biological substrate (as discussed above). A relatively large number of new extraction and injection wells would be installed. The well spacing and orientation (and therefore the overall number of injection wells) would be optimized to achieve the RAOs in the desired duration. Alternative 1a would be more aggressive, achieving RAOs in a shorter time frame, and would use more injection/extraction wells, while Alternative 1b would use a more moderate number of wells. The exact number of wells and flow rates required would be estimated via groundwater modeling. To reduce the cost of injection, injection trenches or shallow injection wells could also be used.
- River protection: Biological reducing zones would be created upgradient of the river. Wells would be installed near the river that would function as either injection or extraction wells that when paired together would allow injection and distribution of a biological substrate. For the southern plume, the In Situ Redox Manipulation (ISRM) wells could serve this purpose, and for the northern plume, an additional line of injection wells would be installed. To prevent reduced water containing secondary byproducts of the biological reductive reactions and low dissolved oxygen from reaching the Columbia River, a line of sparge wells injecting either water saturated with oxygen, or injecting air alone, would be placed adjacent to the river. The length of the sparge barrier would parallel the length of the reducing zone.
- Ex situ treatment: No ex situ treatment would be required in this RAA. All extracted groundwater would be amended with a biological substrate and reinjected. Biological reduction of the hexavalent chromium would occur in situ.
- Horn area: Monitored natural attenuation (MNA) would be used to manage the plume in the Horn area, since the current hexavalent chromium groundwater concentrations are low (<100 μg/L). This would include continued monitoring of wells in the Horn area, along with development of a contingency plan, in case conditions worsen.

Advantages:

- The source areas would be treated aggressively, minimizing the potential for continued contamination of the aquifer.
- Because the reductant would be delivered to the aquifer, rather than the contaminant being removed from the aquifer, in situ treatment could remediate the plume faster than extraction and treatment.
- Organic reductants are several times less expensive than chemical reductants.

Disadvantages:

- Formation of a reduced zone in situ would create secondary byproducts, especially manganese and iron, which would re-precipitate with time once oxidized conditions were encountered. Where time is not available (i.e., in a reduced zone adjacent to the river), oxidation would be required.
- There is uncertainty regarding the ability of a barrier approach to achieve the river RAO quickly.

- Delivery of injected or infiltrated amendments is never uniform, so the subsurface might not be uniformly treated. This could require additional time for treatment.

A2.0 ALTERNATIVE 2 – COMBINATION BIOLOGICAL AND PUMP-AND-TREAT

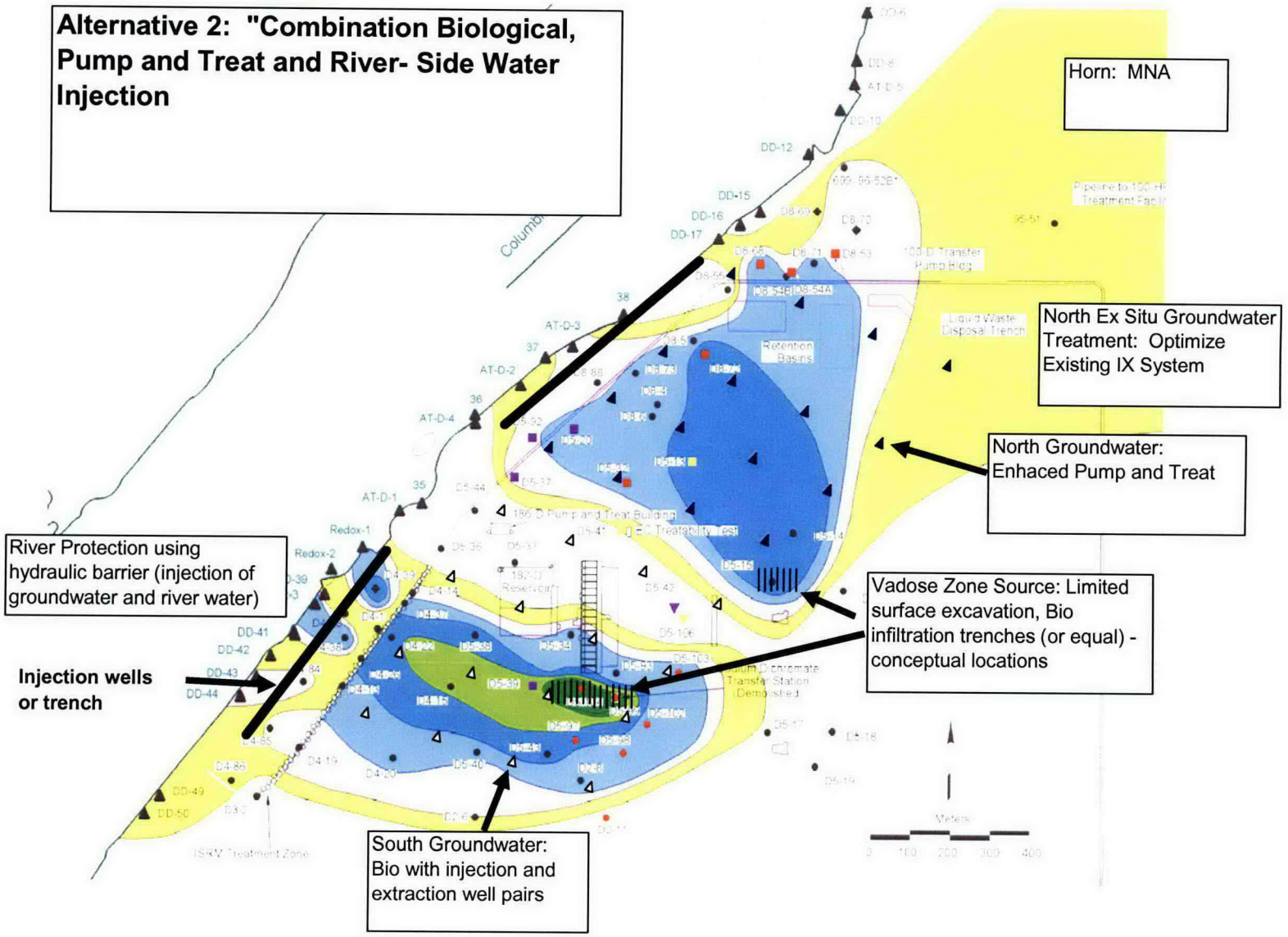
Summary:

In this RAA, the southern plume would be treated with in situ biological treatment and the northern plume would be treated with enhanced pump-and-treat (i.e., enhanced with higher than existing extraction rates). It includes infiltration of biological substrate for the vadose zone source areas, and injection of groundwater/river water to protect the river. Figure A-2 illustrates the components.

Components:

- Vadose zone source areas: Bioremediation via infiltration of an organic substrate as well as limited excavation would be used to treat the known vadose sources of hexavalent chromium in both the northern and southern plumes. The approach used would be the same as discussed for Alternative 1.
- Groundwater plume: The southern plume would be treated using biological treatment as discussed for Alternative 1. The ISRM wells would also be used as injection or extraction wells for this treatment. The northern plume would be remediated using the existing extraction well network that would be expanded by installing additional extraction/injection wells, to extract and flush groundwater with hexavalent chromium. The exact number of wells and flow rates required would be determined via groundwater modeling.
- River protection: A system of vertical wells, horizontal wells, or a horizontal trench would be used to inject treated groundwater and river water as close to the river as is practical. The injection water would create a hydraulic barrier, reducing the potential for migration of contaminated groundwater to the river. The flow rate would be high enough to create a mound so the flow of contaminated groundwater to the river would be reduced. The injections would only be performed during the times of the year that the river level is low and there is a natural hydraulic gradient to the river. During high river stage, it would not be needed since the natural gradient is away from the river. Upgradient extraction and/or in situ treatment would be performed as part of the other components, so the natural flux of groundwater to the river would be reduced. The introduction of clean, oxygenated water would also serve to meet the dissolved oxygen requirement for groundwater discharging to the river. The exact number of wells and flow rates required would be determined via groundwater modeling.
- Ex situ treatment: For the northern plume, ion exchange (IX) would be used to treat extracted groundwater. The existing ex situ treatment systems would be upgraded and expanded. The actual flow rate and concentration of chromium to be treated would be estimated via groundwater modeling.
- Horn area: MNA would be used to manage the plume in the Horn area.

Figure A-2. Alternative 2.



Advantages:

- The source areas would be treated aggressively, minimizing the potential for continued contamination of the aquifer.
- For the southern plume, remediation could occur more quickly than if pump-and-treat was used, as discussed for Alternative 1.
- For the northern plume, where concentrations are much lower, enhanced pump-and-treat might be adequate to achieve the RAOs.
- The use of existing infrastructure would be maximized.
- There is more certainty about achieving the river protection RAO quickly than in Alternative 1.

Disadvantages:

- Same as Alternative 1.
- Pump-and-treat of the northern plume could take more time than anticipated due to heterogeneity in the subsurface and non-uniform flushing.

A3.0 ALTERNATIVE 3 – ALL PUMP-AND-TREAT

3a: Optimize and expand existing IX system(s).

3b: Ferrous iron reduction for ex situ treatment.

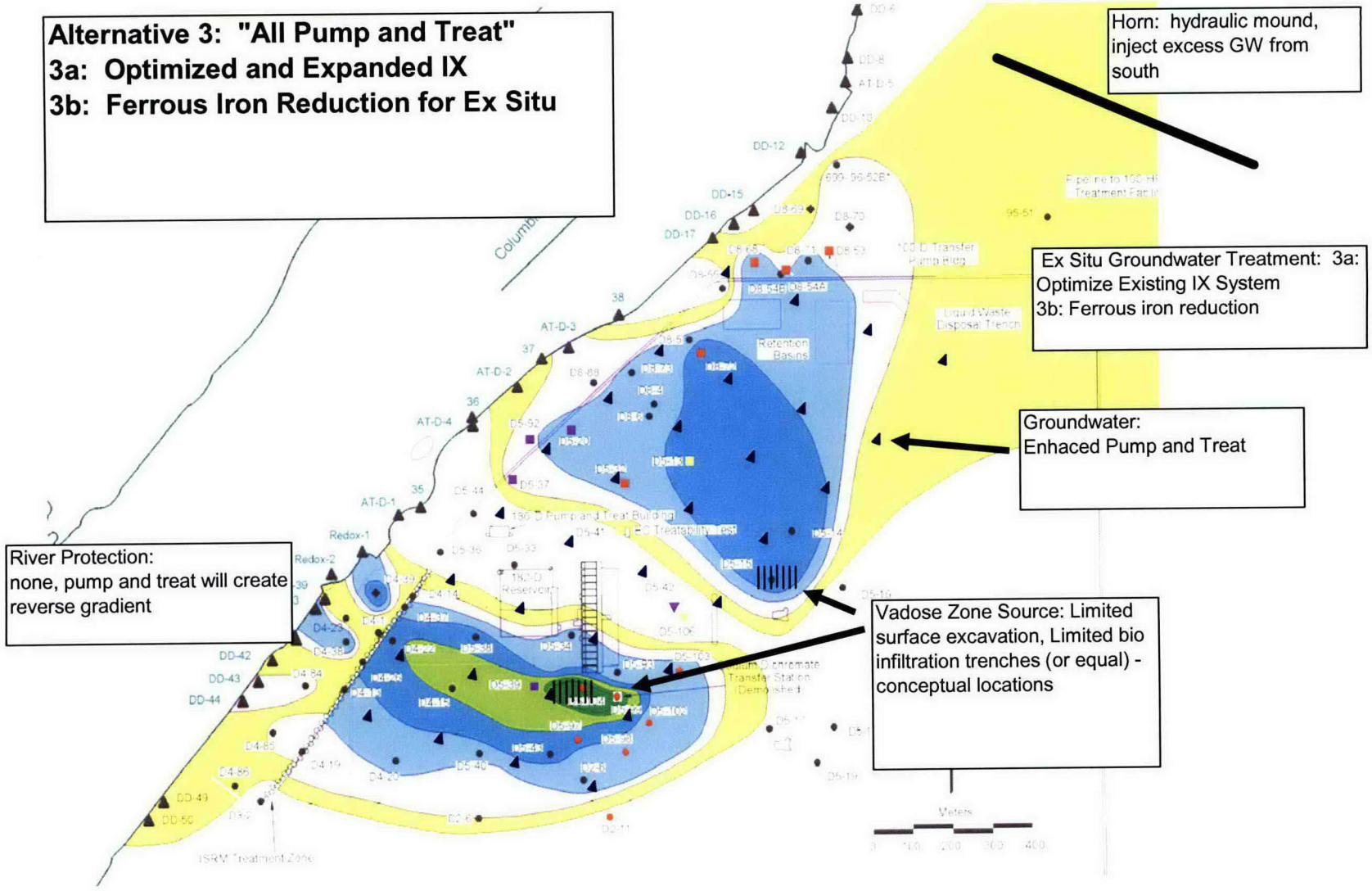
Summary:

This RAA uses expanded pump-and-treat systems to extract the chromium mass in the groundwater and to protect the river. The same approach would be used for the northern and southern plumes. Figure A-3 illustrates the components.

Components:

- Vadose zone source areas: Targeted bioremediation via infiltration of limited quantities of an organic substrate (as discussed above in Alternative 1) would be used so organic substrate would not accumulate in the groundwater and potentially foul the existing treatment systems. Limited excavation as discussed for Alternative 1 would also be used.
- Groundwater plume: Expanded and aggressive pump-and-treat. A relatively large number (possibly on the order of 15) of new extraction and injection wells would be installed to flush hexavalent chromium from the subsurface. The exact number of wells and flow rates required would be determined via groundwater modeling.
- River protection: No unique system would be provided for river protection. The pump-and-treat system would extract enough groundwater from wells close to the river that the gradient would be reversed (groundwater elevations inland would be lower than the river stage) at all times of the year.

Figure A-3. Alternative 3.



- Ex situ treatment: Alternative 3a would use upgraded and expanded IX systems to treat extracted groundwater. Alternative 3b would use a new ferrous iron reduction system. The actual flow rates and concentrations of hexavalent chromium to be treated would be estimated via groundwater modeling.
- Horn area: Excess treated groundwater would be injected in inland wells along the north edge of the northern plume and/or in the 100-HR-3. This would decrease the potential for contaminated groundwater to discharge to the river or migrate north.

Advantages:

- The source areas would be treated, although not as aggressively as Alternative 2, reducing the potential for continued contamination of the aquifer.
- Use of existing infrastructure would be maximized.
- Would use pump-and-treat technology, which is familiar to the site stakeholders.

Disadvantages:

- Pumping and treatment of the plumes could take more time than approaches that also use in situ treatment.
- Ex situ treatment would likely to be more expensive than in situ biological treatment.
- Ex situ treatment could create more residuals requiring disposal, depending on the final configuration of the systems.
- There is uncertainty regarding the ability to reverse the gradient to the river by just pumping, particularly during low river stage times of the year.

A4.0 ALTERNATIVE 4 – AGGRESSIVE TREATMENT INCLUDING IN SITU CHEMICAL REDUCTION

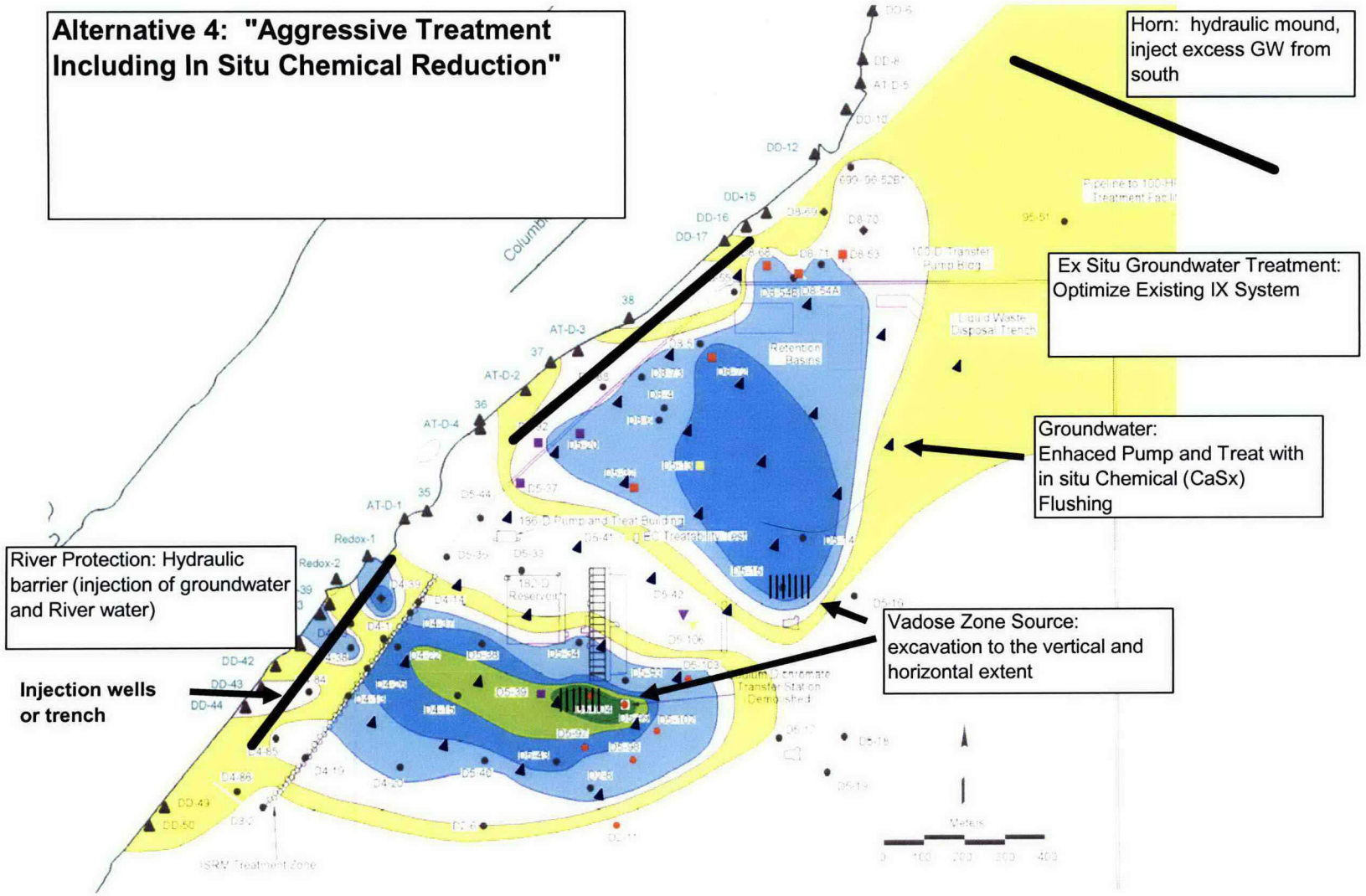
Summary:

This RAA uses an aggressive approach to achieve the RAOs as quickly as possible. It includes excavation of vadose zone sources, aggressive pump-and-treat coupled with chemical reductant injection to remediate groundwater, and injection of groundwater/river water to protect the river. The same approach would be used for the northern and southern plumes. Figure A-4 illustrates the components.

Components:

- Vadose zone source areas: An aggressive program of identifying vadose zone source areas, along with excavation and disposal at the Environmental Restoration Disposal Facility (ERDF), would be used to remove hexavalent chromium mass from the vadose zone. Such an approach could be completed fairly quickly.
- Groundwater plume: A relatively large number (possibly on the order of 25) of new extraction and injection wells would be installed to flush hexavalent chromium from the subsurface. A chemical reductant, such calcium polysulfide, would also be injected into the water to promote in situ reduction of the hexavalent chromium. The exact number of wells and flow rates required would be determined via groundwater modeling.

Figure A-4. Alternative 4.



- River protection: A system of vertical wells, horizontal wells, or a horizontal trench would be used to inject treated groundwater or river water as close to the river as is practical. This approach is the same as in Alternative 2.
- Ex situ treatment: This RAA would use upgraded and expanded IX systems to treat extracted groundwater. The actual flow rates and concentrations of hexavalent chromium to be treated would be estimated via groundwater modeling.
- Horn area: Excess treated groundwater would be injected in inland wells along the north edge of northern plume and/or in the 100-HR-3. This would decrease the potential for contaminated groundwater to discharge to the river or migrate north.

Advantages:

- The source areas would be treated aggressively, reducing the potential for continued contamination of the aquifer.
- The use of chemical reductant coupled with pump-and-treat would reduce the time to achieve RAOs.

Disadvantages:

- Excavation and disposal would likely be more expensive than in situ treatment.
- Ex situ treatment would likely be more expensive than in situ biological treatment.
- In situ chemical reductants are more expensive than in situ biological substrates.
- Ex situ treatment would create more residuals that must be disposed.

A5.0 ALTERNATIVE 5 –OPTIMIZED USE OF EXISTING FACILITIES

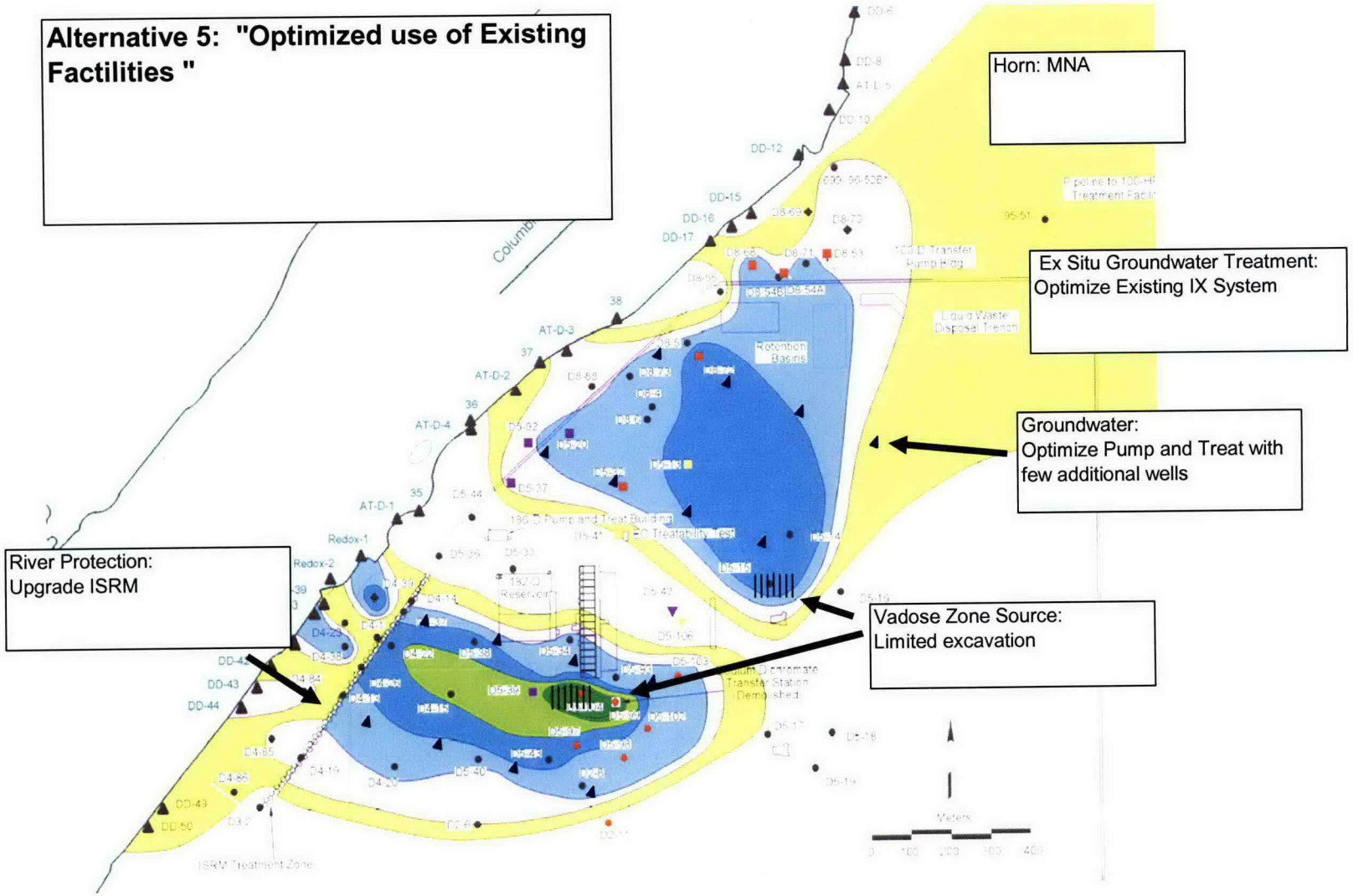
Summary:

This RAA would optimize existing pump-and-treat and ISRM systems. A few additional wells would be added to the pump-and-treat system and the IX systems would be optimized. The existing ISRM would be upgraded for protection of the river and aeration would be provided as needed. Vadose zone contaminated soil would be excavated under the existing program. The same approach would be used for the northern and southern plumes. Figure A-5 illustrates the components.

Components:

- Vadose zone source areas: A modest program of identifying vadose zone source areas, along with excavation and disposal at the ERDF, would be used to remove hexavalent chromium mass from the vadose zone.
- Groundwater plume: A few additional extraction and injection wells would be installed in hot spot areas to more effectively remove hexavalent chromium from the subsurface.
- River protection: The ISRM barrier in the southern plume would be upgraded with the injection of zero-valent iron (or equal) to help protect the river. No system would be provided for river protection in the northern plume. Oxidation would be provided between the ISRM barrier and the river as needed to meet the RAO for dissolved oxygen.

Figure A-5. Alternative 5.



- Ex situ treatment: The existing IX treatment systems would be optimized to treat extracted groundwater. Additional capacity would likely be unnecessary.
- Horn area: MNA would be used to manage the plume in the Horn area, as discussed for Alternative 1.

Advantages:

- The source areas would be treated, although not aggressively, reducing the potential for continued contamination of the aquifer.
- Use of existing infrastructure would be maximized.
- Pump-and-treat technology would be used, which is familiar to the site stakeholders.

Disadvantages:

- Pump-and-treat of the plumes could take more time than anticipated.
- Ex situ treatment would likely be more expensive than in situ biological treatment.
- Ex situ treatment would create more residuals that must be disposed.
- There is uncertainty regarding the ability of the ISRM barrier to protect the river (although pilot tests are currently underway to enhance it) and it does not extend to the northern plume.

A6.0 ALTERNATIVE 6 – ALL BARRIERS

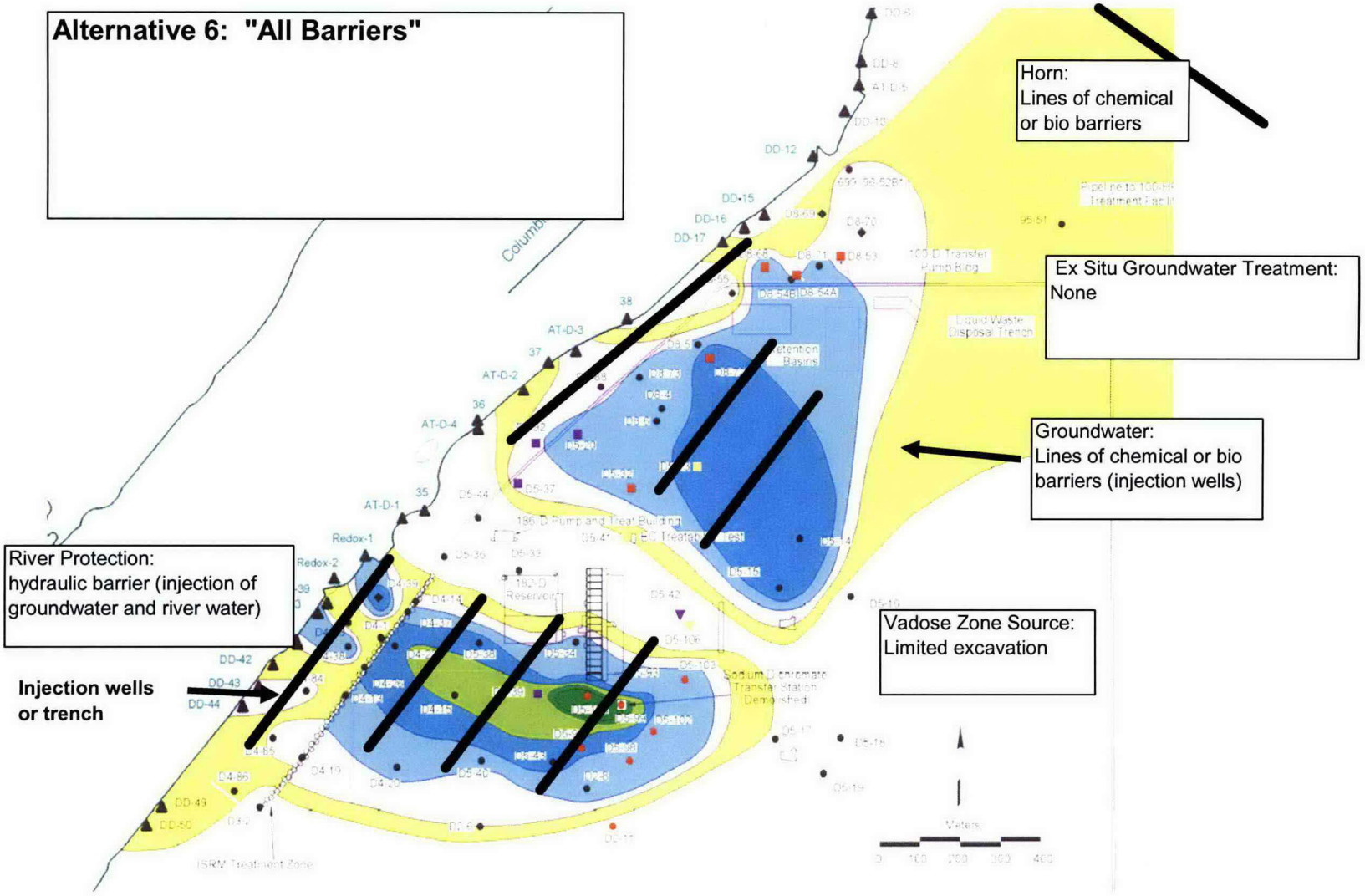
Summary:

This RAA would use a series of in situ bio-barriers. Vadose zone contaminated soil would not be addressed. The same approach would be used for the northern and southern plumes. Figure A-6 illustrates the components.

Components:

- Vadose zone source areas: The excavations currently ongoing as part of the River Corridor Contract program would continue.
- Groundwater plume: In situ bio-barriers comprised of injection and extraction well pairs would be installed. Biological substrate (i.e., carbon source) would be injected to create reducing zones. Once reducing conditions were created, the injection of the biological substrate would only be needed infrequently. Contaminated groundwater would be allowed to flow through the barriers and hexavalent chromium would be reduced to trivalent chromium. The number of barriers needed would be determined via modeling. The ISRM wells would be used as one line of barrier wells.
- River protection: A system of vertical wells, horizontal wells, or a horizontal trench would be used to inject river water as close to the river as is practical. This approach is the same as in Alternative 2.
- Ex situ treatment: None would be required since any groundwater extracted would be reinjected along with biological substrate (and treated in situ).

Figure A-6. Alternative 6.



- Horn area: A bio-barrier would be also created on the north side of the northern plume to reduce the potential for migration of hexavalent chromium to the north.

Advantages:

- This RAA would have potentially lower cost because fewer wells would be needed.

Disadvantages:

- The source areas would not be treated directly, thus achieving the working RAO of compliant groundwater by 2020 would be unlikely.
- This RAA would rely on natural groundwater gradients to flush the contaminated groundwater through the treatment barriers. This could be hampered by changes in groundwater flow direction.

A7.0 ALTERNATIVE 7 – NO ADDITIONAL ACTIONS – STATUS QUO

Summary:

This RAA uses the existing systems as they are. It includes the existing pump-and-treat system to extract the hexavalent chromium mass via groundwater. The existing ISRM barrier, without upgrading, would be used to protect of the river. Shallow vadose zone contaminated soil would be excavated under the current River Corridor Contract program. Figure A-7 illustrates the components. This RAA is put forth as a base case with which to compare other RAAs; it is not capable of achieving short-term or long-term working RAOs for the 100-D Area.

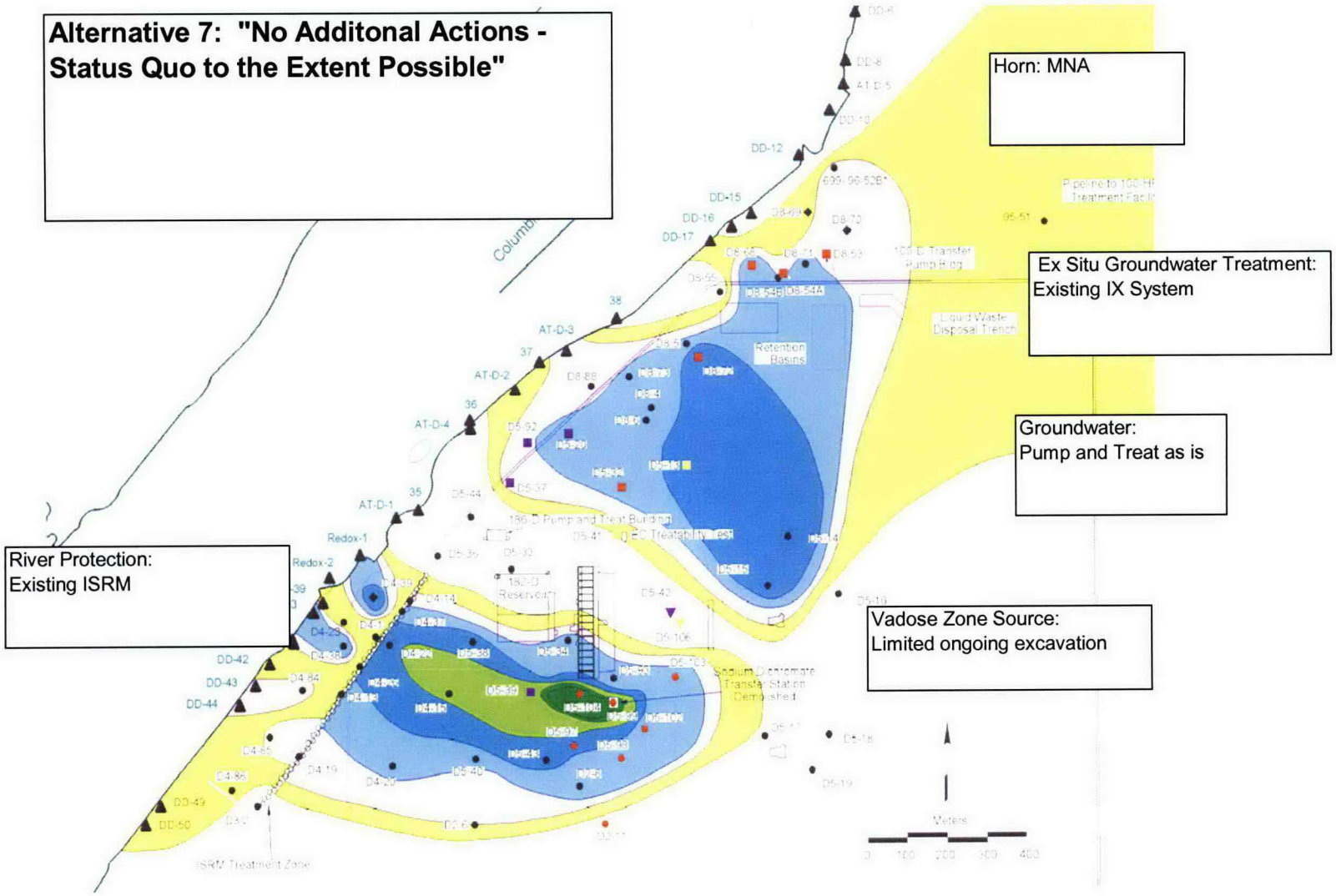
Components:

- Vadose zone source areas: The excavations currently ongoing as part of the River Corridor Contract program would continue.
- Groundwater plume: The existing pump-and-treat system would be used as is.
- River protection: The ISRM would be used as is.
- Ex situ treatment: The existing IX treatment systems would be used as is.
- Horn area: MNA would be used to manage the plume in the Horn area.

Advantages:

- Costs would be low.
- Use of existing infrastructure would be maximized.
- Known technologies would be used.
- Identified source areas would be excavated.

Figure A-7. Alternative 7.



Disadvantages:

- Some source areas would not be treated.
- Pumping and treatment of the plumes at the current rate would not likely achieve the working RAO of remediating groundwater by 2020. The current flushing rate is not likely to be adequate to remove the hexavalent chromium mass by this date.
- Contamination above protection standards would likely discharge to the river.
- Ex situ treatment would likely be more expensive than in situ biological treatment.
- Ex situ treatment would potentially create more residuals that must be disposed.
- The ISRM as it is does not provide adequate protection of the river.

A8.0 ALTERNATIVE 8 – WETLANDS TREATMEN

Summary:

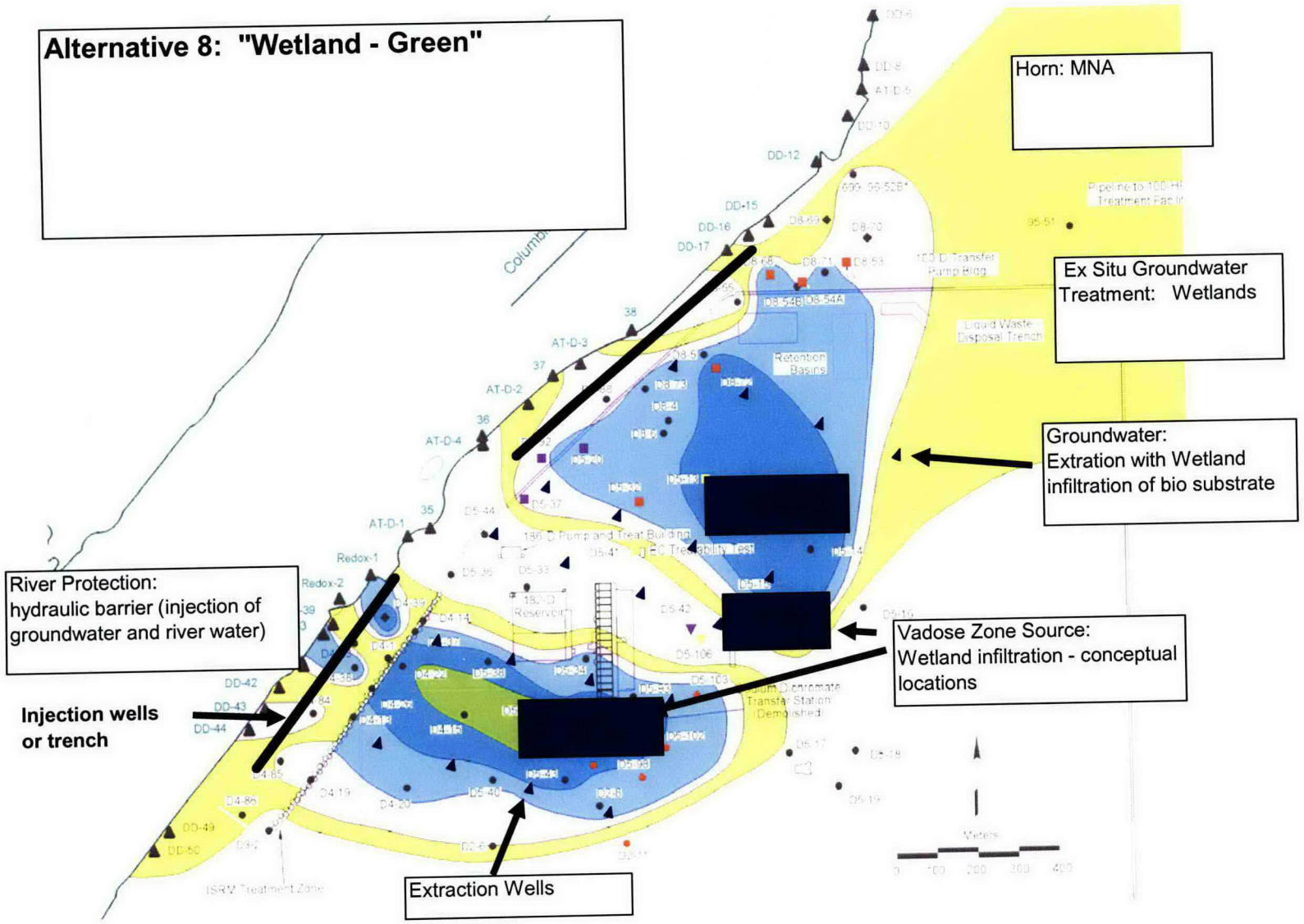
This RAA uses engineered subsurface flow wetlands as the primary treatment method for hexavalent chromium in all the media of concern (Figure A-8). Groundwater would be extracted from both the northern and southern plumes and passively treated by one or more wetlands to reduce hexavalent chromium in the effluent to below 5 to 10 μg/L. The hexavalent chromium removal process in subsurface flow wetlands is primarily based on oxidation-reduction chemistry, but also includes adsorption, direct uptake by plants, and other mechanisms. When hexavalent chromium enters the reducing environment produced in a subsurface flow wetland, it is reduced to trivalent chromium and precipitated as chromium hydroxides or other insoluble phases.

Suspected vadose zone sources and underlying groundwater hot spots would be bioremediated by targeted infiltration of treated effluent from the wetlands. The treated wetland effluent would be amended, as necessary, with biological substrate prior to reinfiltration to expedite remediation of the targeted vadose zone source areas. Groundwater would be addressed by in situ bio-barriers.

Components:

- Vadose zone source areas: No excavation of deep (>10 ft below ground surface [bgs]) vadose zone contamination would be conducted. Suspected vadose zone sources and underlying groundwater hot spots would treated by targeted infiltration of clean wetland effluent amended with biological substrate.
- Groundwater plume: Additional extraction wells would be installed to ensure hydraulic capture of the plume hot spots below vadose zones being treated by wetland effluent. In addition, in situ bio-barriers would be installed as described for Alternative 6.
- River protection: A system of vertical wells, horizontal wells, or a horizontal trench would be used to inject river water as close to the river as is practical, as described for Alternative 2.
- Ex situ treatment: Passive treatment would occur in the engineered subsurface flow wetlands.

Figure A-8. Alternative 8.



- Horn area: MNA would be used to address the potential migration of low concentrations of residual hexavalent chromium to the north

Advantages:

- Subsurface flow-constructed wetlands have been shown to be effective for removing hexavalent chromium along with nitrate and other reduction/oxidation-sensitive constituents that are present at the 100-D Area.
- Wetlands would be a potentially low cost and sustainable RAA. Cost per acre decreases with the total acreage of the wetland.

Disadvantages:

- The potential for clogging and infiltration rates of treated effluent through the vadose zone are uncertain.
- Operation and maintenance requirements are not well understood.

APPENDIX B

LIST OF TECHNOLOGY SCREENING MEETING ATTENDEES

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Table B-1. List of Technology Screening Meeting Attendees, June 4-6, 2008.

Name	Title	Organization	City, State
Jonathan Blount, Ph.D.	Project Manager	CH2M Hill, Inc.	Boston, MA
Andrew Esparza	Engineer	Fluor Hanford, Inc. Groundwater Project	Richland, WA
Brian Esparza	Engineer	Fluor Hanford, Inc. Groundwater Project	Richland, WA
Paul Favara, P.E.	Principal Technologist	CH2M Hill, Inc.	Gainesville, FL
David Forehand	Engineer	Fluor Hanford, Inc. Groundwater Project	Richland, WA
James Hanson, L.G., L.H.G.	100-D, -H, -K, -B/C, and -F Areas Groundwater Project Lead	U.S. Department of Energy, Richland Operations Office Groundwater Project	Richland, WA
Jim Harrington, P.E.	Vice President, Engineering	Alexco Resource Corp.	Denver, CO
Ronald Jackson, R.G., R.H., R.E.G.	Remedial Action Lead	Fluor Hanford, Inc. Groundwater Project	Richland, WA
Jim Mavis	Principal Technologist	CH2M Hill, Inc.	Bellevue, WA
Ellen Moyer, Ph.D., P.E.	Principal Technologist	CH2M Hill, Inc.	Boston, MA
Jeffrey Riddelle, P.E., P.M.P.	Engineering Manager/Chief Engineer	Fluor Hanford, Inc. Groundwater Project	Richland, WA
Doug Sherwood	Owner	Rivers Edge Environmental	West Richland, WA
David Shrimpton, P.E.	100-HR-3 Project Manager	Fluor Hanford, Inc. Groundwater Project	Richland, WA
Thomas Simpkin, Ph.D., P.E.	Principal Technologist	CH2M Hill, Inc.	Denver, CO
Chris Sutton, Ph.D.	Senior Consulting Environmental Engineer	Fluor Hanford, Inc. Groundwater Project	Richland, WA
Matthew Tonkin	Senior Hydrogeologist	S.S. Papadopulos & Associates	Bethesda, MD

L.G. = Licensed Geologist
L.H.G. = Licensed Hydrogeologist
P.E. = Professional Engineer
Ph.D. = Doctor of Philosophy
P.M.P. = Project Management Professional
R.E.G. = Registered Engineering Geologist
R.G. = Registered Geologist
R.H. = Registered Hydrologist

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APPENDIX C

SENSITIVITY ANALYSIS OF THE DECISION SCORING WEIGHTS

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APPENDIX C
SENSITIVITY ANALYSIS OF THE DECISION SCORING WEIGHTS

When the meeting participants evaluated scores, it was recommended that a sensitivity analysis be performed by varying the weights of each scorer. The different scenarios evaluated are presented in Table C-1. To complete this sensitivity analysis, the data entered into the original scoring sheet needed to be reformatted into a database flat file to more efficiently evaluate results based on different weighting scenarios and avoid the manual entry of each scenario into the Criterion Decision Plus software (Microsoft Excel® data were used to rank alternatives evaluated in the sensitivity analysis).

In order for the calculations to be completed without returning a "#VALUE" error, the cells that were left blank by some scorers needed to be filled with actual values. A total of 429 of the 4,950 scores, or 8.67%, were left blank when the scorer did not have an opinion or did feel knowledgeable enough to render an opinion on that particular item. For entries that were left blank, the score of another individual in the same scoring group was applied to the blank cell. So, for example, if scorer "CH2M HILL 4" had a blank cell in their score sheet, the cell value from scorer "CH2M HILL 1" was used to fill in the blank score. The one exception to this approach was the scorer that represented the regulatory agency. Since this scorer was the only one scoring the data from a regulatory perspective, there were no other data that could be used as substitutes. Therefore, blank cells were filled in with a score of 50 (or neutral).

The information below depicts the number of blank cells in the referenced scorer's score sheet, and the source of the values used to fill in those scores.

Table C-1. Blank Cell Data.

Scorer	Blank Cells	Proxy Used
Hanford Engineers	92	DOE RL Project
Lead Regulator Proxy	41	None – a value of 50 was used
CH2M HILL 4	70	CH2M HILL 1
CH2M HILL 3	45	CH2M HILL 1
Consultant 1	89	Consultant 2
Fluor 2	92	Fluor 1

The following sections describe the sensitivity tests.

C1.0 SENSITIVITY TEST 1

This test determines if the revised database, that uses proxy scores, results in similar results as the original scores discussed at the meeting, which were later used to develop alternatives.

Microsoft Excel® is a registered trademark of Microsoft Corporation in the United States and/or in other countries.

Figures C-1 through C-4 show the results for each of the four groups of technologies evaluated. In these figures, the row of data entitled "Decision Analysis Session" refers to the initial numbers developed at the meeting. The row of data entitled "Conversion" represents the results from the revised dataset described above in which blank cells were filled in with proxy values.

While there were minor changes in the total normalized scores, for the most part, the technology rankings were very similar, if not identical, between the two data sets, as summarized below:

- River treatment technologies: There was no change in ranking order (Figure C-1).
- Vadose zone technologies: Institutional controls was ranked 7th in the decision analysis session data set and 11th in the conversion data set (Figure C-2).
- Groundwater technologies: There was no change in ranking order (Figure C-3).
- Ex situ treatment technologies: The only change in ranking order was with technologies ranked 12th and 13th (Figure C-4).

This sensitivity analysis indicated that the technologies ranking in the database file provided essentially equivalent rankings as those developed during the decision analysis meeting. The change in order for the vadose zone treatment technologies (the most divergent results) is relatively insignificant as the six leading ranking technologies did not change. This sensitivity analysis validates the new database as being true to the original rankings (with minor changes) and allows its use for further sensitivity analyses.

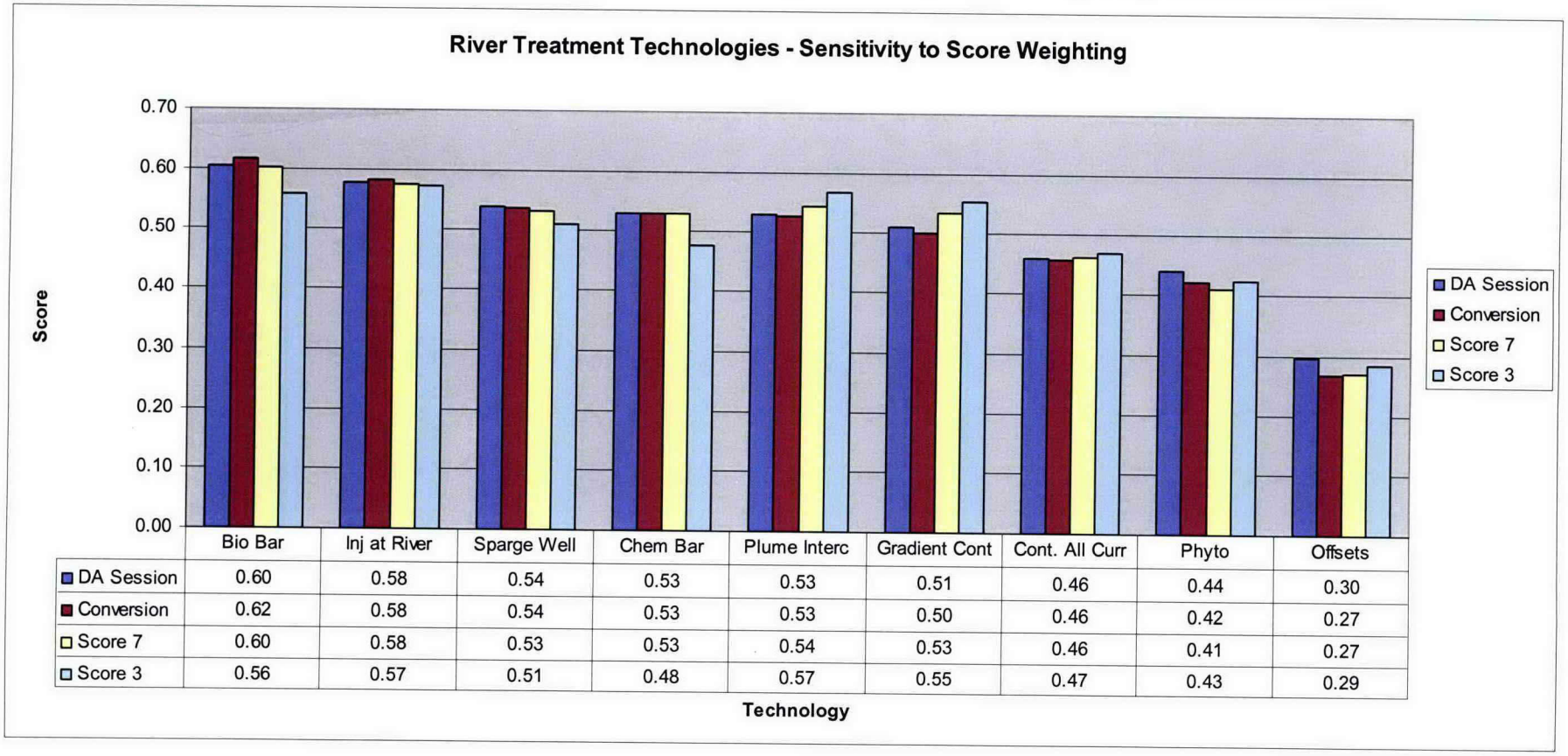
C2.0 SENSITIVITY TEST 2

The second sensitivity test involved changing the weights of the scorers. A total of 11 scorers, equally weighted, were evaluated in the scenarios entitled "Decision Analysis Session" and "Conversion." The Score 7 scenario involved changing score weights, so the four CH2M Hill scores counted as one score and the two Fluor Hanford scores counted as one.

The results of this scenario are presented in Figures C-1 through C-4. In general, the leading technologies for this scenario were the same as for the two previously described scenarios:

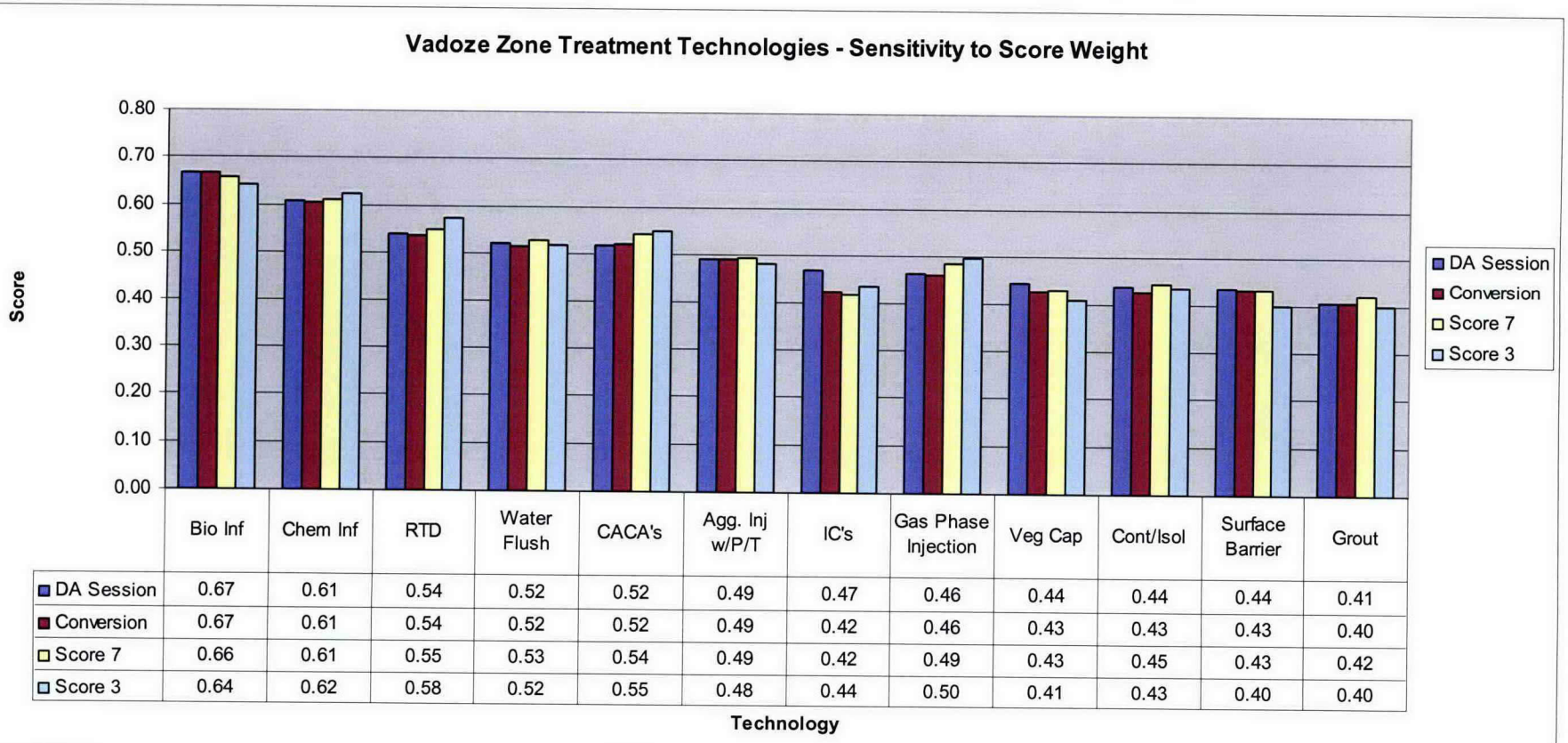
- River treatment technologies: Plume interception was ranked 5th in the decision analysis session and conversion data sets and 3rd in the Score 7 dataset. Scores for the 3rd, 4th, and 5th ranked technologies were very close and minor changes in values caused a change in technology ranking (Figure C-1).
- Vadose zone technologies: The order of ranking of three highest scoring technologies in the Score 7 dataset is the same as in the decision analysis session and conversion data set. Scores for continue all current actions, gas-phase injection, containment/isolation, and grouting all increased slightly over previous iterations and led to changes in technology rankings (Figure C-2).
- Groundwater technologies: There was no change in ranking order (Figure C-3).

Figure C-1. Sensitivity Analysis of River Technologies to Changes in Scoring Weight and Data Source.



	Bio Bar	Inj at River	Sparge Well	Chem Bar	Plume Interc	Gradient Cont	Cont. All Curr	Phyto	Offsets
DA Session	0.60	0.58	0.54	0.53	0.53	0.51	0.46	0.44	0.30
Conversion	0.62	0.58	0.54	0.53	0.53	0.50	0.46	0.42	0.27
Score 7	0.60	0.58	0.53	0.53	0.54	0.53	0.46	0.41	0.27
Score 3	0.56	0.57	0.51	0.48	0.57	0.55	0.47	0.43	0.29

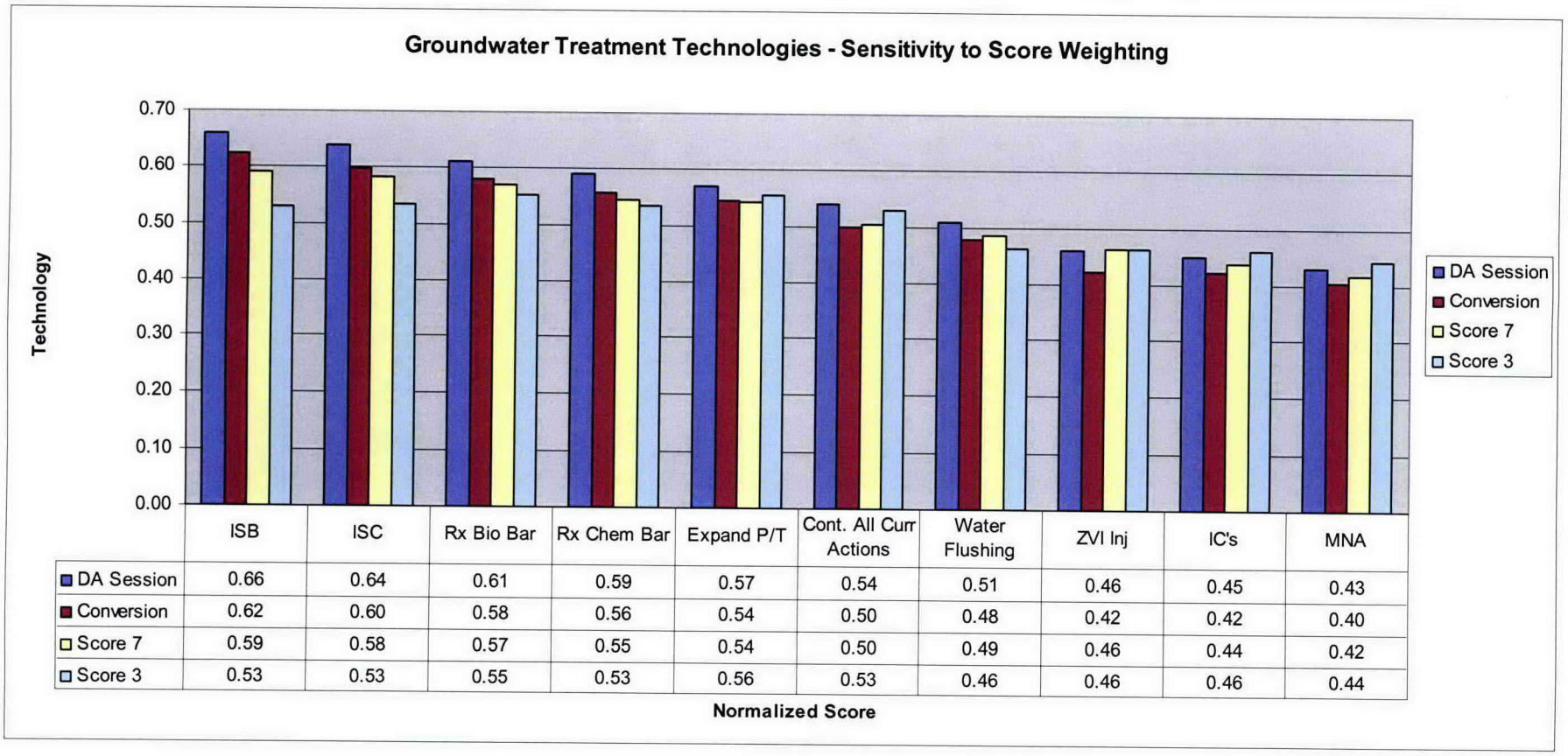
Figure C-2. Sensitivity Analysis of Vadose Zone Technologies to Changes in Scoring Weight and Data Source.



	Bio Inf	Chem Inf	RTD	Water Flush	CACA's	Agg. Inj w/P/T	IC's	Gas Phase Injection	Veg Cap	Cont/Isol	Surface Barrier	Grout
DA Session	0.67	0.61	0.54	0.52	0.52	0.49	0.47	0.46	0.44	0.44	0.44	0.41
Conversion	0.67	0.61	0.54	0.52	0.52	0.49	0.42	0.46	0.43	0.43	0.43	0.40
Score 7	0.66	0.61	0.55	0.53	0.54	0.49	0.42	0.49	0.43	0.45	0.43	0.42
Score 3	0.64	0.62	0.58	0.52	0.55	0.48	0.44	0.50	0.41	0.43	0.40	0.40

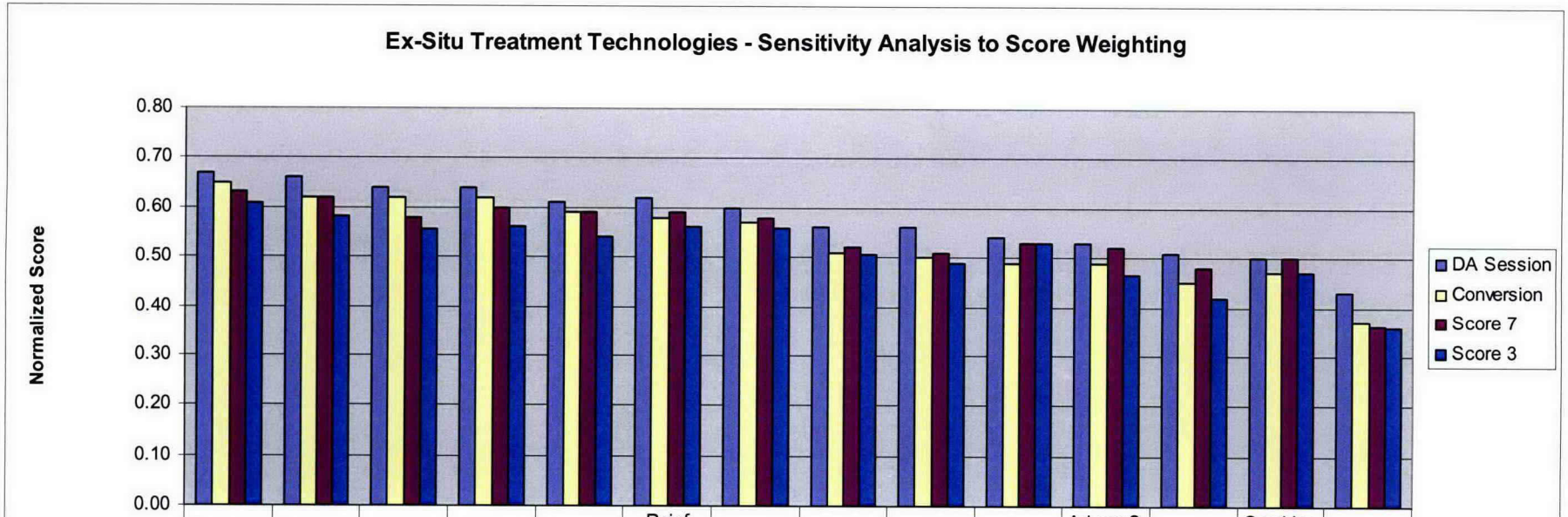
Technology

Figure C-3. Sensitivity Analysis of Groundwater Technologies to Changes in Scoring Weight and Data Source.



	ISB	ISC	Rx Bio Bar	Rx Chem Bar	Expand P/T	Cont. All Curr Actions	Water Flushing	ZVI Inj	IC's	MNA
DA Session	0.66	0.64	0.61	0.59	0.57	0.54	0.51	0.46	0.45	0.43
Conversion	0.62	0.60	0.58	0.56	0.54	0.50	0.48	0.42	0.42	0.40
Score 7	0.59	0.58	0.57	0.55	0.54	0.50	0.49	0.46	0.44	0.42
Score 3	0.53	0.53	0.55	0.53	0.56	0.53	0.46	0.46	0.46	0.44

Figure C-4. Sensitivity Analysis of Ex-Situ Technologies to Changes in Scoring Weight and Data Source.



	Optimize	Reinf Bio	CACA	Fe Red	BioRx	Reinf Chem	RO	Wetlands	Phyto	NPDES	Ads or S Fe	S Treat	Combined WTP	EC
DA Session	0.67	0.66	0.64	0.64	0.61	0.62	0.60	0.56	0.56	0.54	0.53	0.51	0.50	0.43
Conversion	0.65	0.62	0.62	0.62	0.59	0.58	0.57	0.51	0.5	0.49	0.49	0.45	0.47	0.37
Score 7	0.63	0.62	0.58	0.60	0.59	0.59	0.58	0.52	0.51	0.53	0.52	0.48	0.50	0.36
Score 3	0.61	0.58	0.56	0.56	0.54	0.56	0.56	0.51	0.49	0.53	0.47	0.42	0.47	0.36

Technology

- Ex situ treatment technologies: Optimize existing systems and reinfiltration with biological amendments remained the top scoring technologies in this category. The 3rd ranked technology in the previous two scenarios (continue all current actions) ranked 6th in this scenario, and the other technologies were promoted due to this change. There were additional changes in ranking order in technologies ranked 8th through 13th (Figure C-4).

C3.0 SENSITIVITY TEST 3

The final sensitivity test completed involved weighting those who worked at the site as 1, the regulator as 1, and all the contractors and consultants as 1 (see Table C-2). This scenario essentially gives the owning entity one vote, the regulators one vote, and the consultants and contractors one combined vote. This analysis showed the greatest sensitivity to score weights. This scenario had three of the scorers accounting for 67% of the total scoring and the remaining 8 scorers accounting for 33% of the total scoring. While there were more pronounced changes in rankings, the changes in scores was not so pronounced as to make a highly favored technology highly unfavorable or vice versa. It is also important to note that a very small change in score (0.01, or 1%) can change the technology ranking by one or more spots.

C4.0 SENSITIVITY ANALYSIS CONCLUSIONS

The sensitivity analysis did show that the rankings of technologies can change based on the changes in scorers' weights. However, with the exception of sensitivity test 3, the ranking order was not significantly affected. While the ranking order was more affected with sensitivity test 3, the difference in rankings was generally the result of small changes in small numbers.

The sensitivity analysis shows that those technologies that were included in the RAAs (Appendix A) due to their technology ranking from the decision analysis process would still have been chosen given reasonable changes in scoring weights.

Table C-2. Score Weighting Scenarios.

Scorer	Decision Analysis Session Weights	Database Conversion Weights	Score 7 Weights	Score 3 Weights
DOE-RL Project Lead	1	1	1	0.5
Hanford Engineers (4)	1	1	1	0.5
Regulator Proxy	1	1	1	1
Fluor 1	1	1	0.5	0.165
Fluor 2	1	1	0.5	0.165
Consultant 1	1	1	1	0.165
Consultant 2	1	1	1	0.165
CH2M HILL 1	1	1	0.25	0.0825
CH2M HILL 2	1	1	0.25	0.0825
CH2M HILL 3	1	1	0.25	0.0825
CH2M HILL 4	1	1	0.25	0.0825
Total Scores Counted	**11**	**11**	**7**	**3**

APPENDIX D

Modified Groundwater Capital Cost Factors
for AboveGround Facilities

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APPENDIX D
Modified Groundwater Capital Cost Factors for AboveGround Facilities

Capital cost for the three technologies were developed from factors recommended in *Plant Design and Economics for Chemical Engineers* (Peters and Timmerhaus 2003). The recommended factors were adjusted based on assumptions concerning probable working conditions, non-conventional safety and site training requirements and experience from previous construction projects at the site. The original factors and modifications are summarized in Table D-1.

Table D-1. Original and Modified Factors Used for Ex Situ Treatment System Capital Cost Estimates.

Fluid Processing Plant Factor Category	Original Installation Factors (Peters and Timmerhaus 2003)	Modification for Hanford	Basis	Revised Factors
Purchased equipment (after applying scoping contingency[a])	100	None	Not changed	100
Purchased equipment installation	47	1.15	Assumption[b]	54.1
Instrumentation and controls	36	1.15	Assumption[b]	41.4
Piping (installed)	68	1.15	Assumption[b]	78.2
Electrical (installed)	11	1.15	Assumption[b]	12.7
Buildings ($100/ft^2)	-	-	-	-
Yard improvements	10	1.15	Assumption[b]	11.5
Service facilities	70	0.75	Reduced for these technologies[c]	52.5
Land	6	0	No land purchased	0
Engineering and supervision	33	None	Not changed	33
Construction expenses	41	None	Not changed	41
Administrative and miscellaneous[d]	20	None	Not changed	20
Contractor's overhead and profit	22	None	Not changed	22
Contingency	42	None	Not changed	44

NOTE: Original installation factors were obtained from *Plant Design and Economics for Chemical Engineers* (Peters and Timmerhaus 2003).

[a] The scoping contingency accounts for incomplete identification of process equipment at this current early stage of design.

[b] Modifications cover site safety, health physics monitoring, site security, and logistical challenges.

[c] These technologies do not require steam, fuel, or other infrastructure common to self-sufficient industrial facilities. Factor includes portable sanitary facilities, limited imported water, safety, housekeeping, and other necessities.

[d] Miscellaneous administrative costs (assumed percentage) include legal, regulatory, stakeholder requirements and permitting, taxes, bonding and insurance.

REFERENCE

Peters, M. S., and K. D. Timmerhaus, 2003, *Plant Design and Economics for Chemical Engineers*, McGraw-Hill Book Company, New York, New York.

APPENDIX E

CAPITAL AND OPERATION AND MAINTENANCE COST BREAKDOWN TABLES

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Table E-1. Mass Balance – Hexavalent Chromium Ion-Exchange System Offsite Regeneration.

Component		1		2		3		4		5		6		7		8		9		10	
		Wells		System Feed		Single Train Feed		Total Effluent		Final Effluent		Process Water		Backwash		Resin Sluicing		Acid, 93%		Recovered Water	
		mg/L	pound/day	mg/L	pound/day	mg/L	pound/day	mg/L	pound/day	mg/L	pound/day	Average	Peak	Average	Peak	Average	Peak	mg/L	pound/day	Average	Peak
Hexavalent chromium		0.5	9.0	0.5	9.0	0.5	1.5	<0.005		<0.005											
Total chromium		0.5	9.0	0.5	9.0	0.5	1.5	<0.005		<0.005											
Chloride		19	343.4	19	343.4		57.2	19		76.7											
Iron			0		0		0			0											
Sulfate		60	1,084	72.7	1,313.8		219.0			~72.7								12.7	229.5		
Bicarbonate		122	2,204.7	105.8	2,208.3		367.5			105.8											
Nitrate – N		5.87	106		106.1		17.7			~17.7											
Uranium		0.004	0.072		0.072		0.012	0		0											
Sulfuric acid																		13	234.9		
pH		7.5		7.0				7.0		7.0		7.0		7.0		7.0				7.0	
Flow rate	gpm		1,500		1,738		290		1,738		1,500	1.06	70.7 & 167	0.07	70.7	0.99	167		0.0126	1.06	70.7 & 167

gpm = gallons per minute

Table E-2. Equipment List for Hexavalent Chromium Ion-Exchange System with Offsite Regeneration.

Major Equipment and Systems	Equipment Size, metric	Equipment Size, English	Number of Units	Equipment Description	Unit Cost (Dollars)	Total Cost (Dollars)
Feed tank and treated water tank	60,566 L	16,000 gal	2	Vertical, polyethylene tanks: 4.27 m (14 ft) diameter, 4.27 m (14 ft) high, each tank sized for 10 minutes storage at 5,678 L/min (1,500 gpm).	21,000	42,000
Sulfuric acid tank	1,136 L	300 gal	1	Tank sized for two weeks storage of 93% sulfuric acid. Part number VT0300-35, 0.89 m (35 in.) diameter, 2.06 m (81 in.) high.	285	285
Transport totes	1.13 m^2	40 ft^3	420	1.13 m^3 (40 ft^3) totes used for shipment of resin offsite for regeneration. Use rate of 20 totes/week is based on the following calculation: (134 ft^3/column x 1 column/train-week x 6 trains) /40 ft^3/tote . The total quantity is based on a 21 week (144 day turn around for regeneration.	3,861	1,161,620
Bag filter housing	378 L/min	100 gpm	1	Aluminum filter housing to capture fines and other solids generated during backwash. 8.79 kg/cm^2 (125 psi) design pressure, 3.8 to 378 L/min (1 to 100 gpm) flow. The flow rate drives the cost for the housing. The peak backwash flow rate is 71 gpm. Alternatives that provide the required flow rate are more expensive (www.filtersource.com).	780	780
On-line hexavalent chromium analyzer	N/A	N/A	1	Automated optical spectrometer. Skalar Model OPA 2000, with manifolds to accommodate up to six ion exchange trains.	50,000	50,000
IX skids - four columns per skid	946 L/min/train	250 gpm/train	6	Four columns (lead-lag-polish-standby) in each of six skids (trains). Each column will hold approximately 3.79 m^3 (134 ft^3) of resin, with diameter of 1.83 m (6 ft), and the total height approximately 3.35 m (11 ft). Overall skid dimensions (four columns per skid): 3.05 m by 9.15 m (10 ft by 30 ft).	225,000	1,350,000
IX resin (in IX columns system during operation)	3.79 m^3	134 ft^3	24	Purolite A-500 is the resin in current use in the DR-5 system. Resin loading capacity for hexavalent chromium in DR-5 is 3.3 times greater than that of 100-HR-3, which uses Dowex 21K. Quantities were calculated based on a flow rate of 15 bed volumes/hour.	130/ft^3	418,080
IX resin (in totes during regeneration)	1.13 m^3	40 $ft^{\#}$	420	Purolite A-500 is the resin in current use in the DR-5 system. Resin loading capacity for hexavalent chromium in DR-5 is 3.3 times greater than that of 100-HR-3, which uses Dowex 21K. Quantities were calculated based on a flow rate of 15 bed volumes/hour.	130/ft^3	2184,000
					Subtotal Equipment Cost	**$1,861,000**
					Subtotal Totes and Spare Resin Cost	**$3,806,000**

gpm = gallons per minute
IX = ion exchange
psi = pounds per square inch

Table E-3. Capital Cost for Ion Exchange with Offsite Regeneration.

Direct Costs			
Purchased Equipment Cost			
	Factor, %	**Cost, $**	
Defined equipment cost, $		1,861,145	
Scoping contingency	20	372,229	
Subtotal Purchased Equipment Cost, $		**2,233,374**	**2,233,374**
Installation Cost Factors			
	Factor, %	Cost, $	
Installation	54.1	1,208,255	
Instrumentation and controls	41.4	924,617	
Piping	78.2	1,746,498	
Electrical	12.7	283,638	
Building ($100/sq ft)	11,875	1,187,500	
Yard improvements	11.5	256,838	
Service facilities	52.5	1,172,521	
Totes with resin		3,805,620	
Subtotal Installation, $		**10,585,488**	
Subtotal - Direct Plant Cost, $			**12,818,862**
Indirect Costs			
Contracting and Permitting			
	Factor, %	**Cost, $**	
Engineering and supervision	33	737,013	
Construction expenses	41	915,683	
Administrative and miscellaneous	20	466,675	
Contractor's overhead and profit	21	469,009	
Contingency	42	938,017	
Subtotal Indirect Costs, $		**3,506,397**	
Subtotal Fixed Capital Investment, $			**16,325,260**
Total Capital Investment, $			**16,325,260**

Table E-4. O&M Cost for Ion Exchange with Offsite Regeneration.

	Usage Rate	Units	Unit Cost, $	Units	Annual cost, $/yr.
Chemicals					
Sulfuric acid (93%)	235	pound/day	$124	ton	$5,318
Other Consumables					
Purolite A-500 resin (10%/year)	324	ft^3/yr	$130	ft^3	$42,120
Regeneration Costs					
Offsite regeneration (includes shipping)	90	Month	$3,120	tote	$3,369,600
Radiological analysis of resins	90	Month	$1,500	tote	$1,620,000
Electricity					
Rotating equipment	4,512	kWh/day	$0.03	kWh	$49,406
Area lighting	427.5	kWh/day	$0.03	kWh	$4,681
Other miscellaneous	150	kWh/day	$0.03	kWh	$1,643
Labor					
Shift operators	7	Full-time equivalent	$75	hour	$1,092,000
Waste Disposal					
Resin fines	7	ton/yr	$28	ton	$196
Waste Characterization and Monitoring					
Solid waste	52	samples/yr	$1,000	per sample	$52,000
Maintenance					
Maintenance	3	% fixed capital investment			$489,758
Total Operation and Maintenance Cost, $/year		**6,726,722**			

Table E-5. Mass Balance – Hexavalent Chromium Ion Exchange System Onsite Regeneration. (2 sheets).

Component		1		2		3		4		5		6		7		8		9		10		11		12	
		Wells		System Feed		Single Train Feed		Total Effluent		Final Effluent		Process Water		Backwash		Regenerant Flow (10%)		Acid, 93%		Recovered Water		Fast Rinse		Saturated Brine Transfer	
		mg/L	pound/ day	mg/L	poun d/day	mg/L	pound/ day	mg/L	poun d/day	mg/L	pound/ day	Avg.	Peak	Avg.	Peak	Avg.	Peak	mg/L	pound/ day	Avg.	Peak	Avg.	Peak	Avg.	Peak
Hexavalent chromium		0.5	9.0				1.5	<0.005		<0.005															
Total chromium		0.5	9.0				1.5	<0.005		19															
Chloride		19	343.4				57.2			0															
Iron		0	0.0				0.0			~72.7								12.7							
Sulfate		60	1,084.3				180.7			105.8									229.5						
Bicarbonate		122	2,204.7				367.5			63.8															
Nitrate - N		5.87	106.1				17.7			~17.7															
Uranium		0.004	0.072				0.012			~0															
Sulfuric acid																		13	234.9						
pH		7.5		7.0				7.0		7.0		7.0		7.0		7.0				7.0		7.0			
Ferrous chloride																									
Sodium chloride																									
Pre-coat diatomaceous earth																									
Ferric hydroxide																									
Chromic hydroxide																									
Solids (dry weight)	pounds/ day																								
Solids (wet-weight)	pounds/ day																								
Air	scfm																								
Flow rate	pounds/ min																308.4								
Flow rate	gpm		1,500		1,507		251		1,507		1,507	1.06		0.07	70.7	0.85	33.4		0.013		6.5	4.73	200.6	0.29	50

Table E-5. Mass Balance – Hexavalent Chromium Ion Exchange System Onsite Regeneration (2 sheets).

Component		13		14		15		16		17		18		19		20		21		22		23		24	
		Filtrate		Treated Regenerant		Ferrous Chloride (30%)		Regenerant Tank Effluent		Polyelectrolyte		Pre-Coat Slurry		Dewatered Sludge		Air Flow		Slow Rinse		Rock Salt		Diluent for Rock Salt		Saturated Brine Solution (26%)	
		Avg.	Peak	Avg.	Peak	Avg.	Peak	Avg.	Peak	Avg.	Peak	Avg.	Peak	Avg.	Peak	Avg.	Peak	Avg.	Peak	Avg.	Peak	Avg.	Peak	Avg.	Peak
Hexavalent chromium																									
Total chromium																									
Chloride																									
Iron																									
Sulfate																									
Bicarbonate																									
Nitrate - N																									
Uranium	pounds/ day											0.072													
Sulfuric acid																									
pH																									
Ferrous chloride	pounds/ day					437																			
Sodium chloride	pounds/ day																			1,091					
Pre-coat diatomaceous earth	pounds/ day											32.2													
Ferric hydroxide	pounds/ day											111													
Chromic hydroxide	pounds/ day											17.8													
Solids (dry weight)	pounds/ day											161													
Solids (wet-weight)	pounds/ day											517.6													
Air	scfm																117								
Flow rate	pounds/ min																				29.8				114.6
Flow rate	gpm	1.7		1.70	1.70	0.028	2.65	1.7		0.0108	0.30		7.50					0.85	33.4				50	0.29	11.46

gpm = gallons per minute

Table E-6. Equipment List for Hexavalent Chromium Ion Exchange System with Onsite Regeneration.

Major Equipment and Systems	Equipment Size, metric	Equipment Size, English	Number of Units	Equipment Description	Unit Cost (dollars)	Total Cost (dollars)
All equipment				General comment: general assumption assumes maximum failure time for any given equipment is one day.		
Feed tank and treated water tank	60,566 L	16,000 gal	2	Vertical, polyethylene tanks: 4.27 m (14 ft) diameter, 4.27 m (14 ft) high, each tank sized for 10 minutes storage at 5,678 L/min (1,500 gpm).	21,000	42,000
Sulfuric acid tank	1,136 L	300 gal	1	Tank sized for two weeks storage of 93% sulfuric acid. Part number VT0300-35, 0.89 m (35 in.) diameter, 2.06 m (81 in.) high.	285	285
Bag filter housing	378 L/min	100 gpm	1	Aluminum filter housing to capture fines and other solids generated during backwash. 8.79 kg/cm^2 (125 psi) design pressure, 3.8 to 378 L/min (1 to 100 gallons per minute) flow.	780	780
On-line hexavalent chromium analyzer	N/A	N/A	1	Automated optical spectrometer. Skalar Model OPA 2000, with manifolds to accommodate up to six ion-exchange trains.	50,000	50,000
Ion-exchange skids - four columns per skid			6	Four columns (lead-lag-polish-standby) in each of six skids (trains). Each column will hold approximately 3.79 m^3 (134 ft^3) of resin, with diameter of 1.83 m (6 ft) and the total height, approximately 3.35 m (11 ft). Overall skid dimensions (four columns per skid) – 3.05 m by 9.15 m (10 ft by 30 ft).	225,000	1,350,000
Ion-exchange resin	3.79 m^3	134 ft^3	24	Purolite A-500 is the resin in current use in the DR-5 system. Resin loading capacity for hexavalent chromium in DR-5 was superior to that of 100-HR-3, which uses Dowex 21K. Quantities were calculated based on a flow rate of 15 bed volumes/hour.	130/ft^3	418,080
Air blower	3.31 m^3/min @ 15.6C	117 cfm @ 60F	1	Rotary-lobe, positive-displacement blower.	10,839	10,839
Demister			1	15.2-cm (6-in.) Kynar Mesh demister.	507	507
Regenerant treatment tanks - cone bottom	43,532 L	11,500 gal	3	Three cone-bottom treatment tanks (43,532L [11,500 gal]). 3.61 m (142 in.) diameter, 5.45 m (214.5 in.) high.	15,999	47,997
Cone bottom tank stands			3	Stands for cone-bottom tanks.	3,500	10,500
Treated regenerant tank	60,566 L	16,000 gal	1	Vertical polyethylene tank. 4.27 m (14 ft) diameter, 4.27 m (14 ft) high.	21,000	21,000
Ferrous chloride tank	3785 L	1,000 gal	1	Vertical polyethylene tank.	2,754	2,754
Pre-coat slurry feed tank	18,927 L	5,000 gal	1	Vertical polyethylene tank. 2.59 m (8.5 ft) diameter, 3.81 m (12.5 ft) high.	6,875	6,875
Brine feed tank	22,712 liters	6,000 gallons	1	Vertical polyethylene tank sized for storage of saturated sodium chloride solution. 3.05 m (10 ft) diameter, 3.05 m (10 ft) high.	7,740	7,740
Salt saturator	25,741 liters	6,800 gallons	1	Vertical polyethylene tank for preparing brine from rock salt. 3.05 m (10 ft) diameter, 3.66 m (12 ft) high.	8,400	8,400
Polymer feed system	284 liters	75 gallons	1	$27,150 cost from email. Used escalator of 1.24 based on 2004 and 2008 CEPCI indices.	34,000	34,000
Vacuum pre-coat filter system	1.83 m diameter by 2.44 m length	6' diameter by 8' length	1	ALAR Engineering Co. (similar to EIMCO vacuum filters). 1.83 m (6 ft) diameter, 2.44 m (8 ft) long drum.	164,000	164,000
			Subtotal Equipment Cost		**2,175,757**	

gpm = gallons per minute

Table E-7. Capital Cost for Ion Exchange with Onsite Regeneration.

Direct Costs			
Purchased Equipment Cost			
	Factor, %	**Cost, $**	
Defined equipment cost, $		2,175,757	
Scoping contingency	20	435,151	
Subtotal Purchased Equipment Cost, $		**2,610,908**	**2,610,908**
Installation Cost Factors			
	Factor, %	**Cost, $**	
Installation	54.1	1,412,501	
Instrumentation and controls	41.4	1,080,916	
Piping	78.2	2,041,730	
Electrical	12.7	331,585	
Building ($100/sq ft)	14,700	1,470,000	
Yard improvements	11.5	300,254	
Service facilities	52.5	1,370,727	
Subtotal Installation, $		**8,007,715**	
Subtotal - Direct Plant Cost, $			**10,618,623**
Indirect Costs			
Contracting and Permitting			
	Factor, %	**Cost, $**	
Engineering and supervision	33	861,600	
Construction expenses	41	1,070,472	
Administrative and miscellaneous	20	522,182	
Contractor's overhead and profit	21	548,291	
Contingency	42	1,096,582	
Subtotal Indirect Costs, $		**4,099,126**	
Subtotal Fixed Capital Investment, $			**14,717,749**
Total Capital Investment, $			**14,717,749**

Table E-8. Operation and Maintenance Cost for Ion Exchange with Onsite Regeneration.

	Usage Rate	Units	Unit Cost, $	Units	Annual cost, $/mo.
Chemicals					
Sulfuric acid (93%)	235	pound/day	$124	ton	$5,318
Ferrous chloride solution (30%)	437	pound/day	$0.135	pound	$21,533
Rock salt (NaCl)	1,091	pound/day	$75	ton	$14,933
Polyelectrolyte	0.323	pound/day	$1.10	pound	$130
Diatomaceous earth (pre-coat media)	32.2	pound/day	$0.32	pound	$3,761
Other Consumables					
Purolite A-500 resin (10%/year)	324	ft^3/yr	$130	ft^3	$42,120
Electricity					
Rotating equipment	4,895	kWh/day	$0.03	kWh	$53,600
Area lighting	529	kWh/day	$0.03	kWh	$5,793
Other miscellaneous	150	kWh/day	$0.03	kWh	$1,643
Labor					
Shift operators	11	Full-time equivalent	$75	hour	$1,716,000
Waste Disposal					
Process solids	112	ton/yr	$28	ton	$3,136
Waste Characterization					
Solid waste	5	samples/yr	$1,000	per sample	$5,000
Maintenance					
Maintenance	3	% fixed capital investment			$441,532
Total Operation and Maintenance Cost, $/year					**2,314,499**

Table E-9. Mass Balance - Ferrous Chloride System. (2 sheets)

Component		1		2		3		4		5		6		7		8		9		10		11	
		Wells		Feed		2nd Hexavalent Chromium Reactor		1st Oxidation Reactor		3rd Oxidation Reactor		Clarifier Effluent		Final Effluent		HCl 35%		$FeCl_2$ 30%		$FeCl_2$ 30%		NaOH 25%	
		mg/L	pound/ day		pound/ day	mg/L	pound/ day							mg/L	pound/ day		pound/ day		pound/ day				
Hexavalent chromium		0.5	9.0		9.0	0.5	9.0							<0.005									
Total chromium		0.5	9.0		9.0	0.5	9.0							<0.005									
Chloride		19	343	65	1219	102	1912							102			876		692.2				
Iron			0		0	29	545							<0.01					545.3				
Sulfate		60	1,084	58	1,084	58	1,084							58									
Bicarbonate		122	2,205	38	721	38.3	1,721							38									
Nitrate - N		5.87	106		106	6	106							6									
Uranium		0.004	0.072		0.072	0.004	0.072							~0									
Ferrous chloride																			1,237				
Sodium hydroxide																							3,603
Hydrochloric acid																	2,573						
pH		7.5		6.0		6.0		7.5		7.5		7.5		7.5									
Solids (dry weight)	pounds/ day																						
Solids (wet-weight)	pounds/ day																						
Air	scfm																						
Flow rate	pounds/ day		18,014,400		18,763,440		18,766,613		18,830,264								2,181		3,173				3,603
Flow rate	gpm		1,500		1,562		1,563		1,568						1,499.8		0.18		0.264	(as needed)			338.8
Properties																SG	1.18	SG	1.3			S.G.	1.275

Table E-9. Mass Balance - Ferrous Chloride System. (2 sheets)

Component		12		13		14		15		16		17		18		19		20		21		22	
		Air		NaOH 25%		Return Flow		Sludge Recycle		Filter Aid		Sludge Blowdown		Flocculant		Filter Backwash		Solid Waste		Pre-Coat			
		mg/L			pound/ day		pound/ day		pound/ day				pound/ day		pound/ day	Avg.	Peak		pound/ day		pound/ day		
Hexavalent chromium																							
Total chromium																							
Chloride																							
Sulfate																							
Bicarbonate																							
Nitrate - N																							
Uranium																			0.072				
Ferrous chloride																							
Sodium hydroxide																							
Pre-coat diatomaceous earth																			212		212		
Ferric hydroxide													1,043						1,043				
Chrome hydroxide													17.9						17.9				
pH																							
Solids (dry weight)	pounds/ day										2.65		1,061		18				1,273		212		
Solids (wet-weight)	pounds/ day										1,060		26,527						3,638		2,122		
Air	scfm		2,025																				
Flow rate	pounds/ day						746,859		60,048		1,060		25,466			720,576			2,365		2,122		
Flow rate	gpm				0.235		62		5		0.088		2.120		0.6	60	720		0.20		0.18		

gpm = gallons per minute

Table E-10. Equipment List for Ferrous Chloride Treatment System for Hexavalent Chromium Removal.

Major Equipment and Systems	Equipment Size, metric	Equipment Size, English	Number of Units	Equipment Description	Unit Cost (dollars)	Total Cost (dollars)
Feed tank and treated water tank	60,566 L	16,000 gal	2	Vertical, polyethylene tanks. 4.27 m (14 ft) diameter, 4.27 m (14 ft) high, each tank sized for 10 minutes storage at 5,678 L/min (1,500 gallons per minute).	21,000	42,000
Hydrochloric acid tank	24,605 L	6,500 gal	1	Vertical, polyethylene tank, sized for tank truck shipments. 3 .05 m (10 ft) diameter, 3.66 m (12 ft) high.	8,825	8,825
Ferrous chloride tank	24,605 L	6,500 gal	1	Vertical, polyethylene tank, sized for tank truck shipments. 3.05 m (10 ft) diameter, 3.66 m (12 ft) high.	8,825	8,825
First hexavalent chromium reactor	32,554 L	8,600 gal	1	Fiberglass reinforced plastic tank. 5 minutes hydraulic residence time (working volume) with 10% percent freeboard.	36,026	36,026
Second hexavalent chromium reactor	67,380 L	17,800 gal	1	Fiberglass reinforced plastic tank. 10 minutes hydraulic residence time (working volume) with 10% percent freeboard. 3.9 m (13 ft) diameter, 5.49 m (18 ft) high.	55,741	55,741
Sodium hydroxide tank	18,927 L	5,000 gal	1	Horizontal welded steel tank, sized for 17,034-L (4,500-gal) truckloads. 1.83 m (6 ft) diameter, 7.31 m (24 ft) long.	5,500	5,500
Oxidation reactors	213,876 L	56,500 gal	3	Fiberglass reinforced plastic tanks - 30-minutes hydraulic residence time (working volume) each with 20% freeboard. 7.62 m (25 ft) diameter, 4.88 m (16 ft) high.	111,363	334,089
Blower	57.3 m^3/minutes @21.1 C	2,025 scfm	1	Rotary-lobe, positive-displacement blower, common to all three air-sparged oxidation reactors.	40,232	40,232
Demister			3	15.2-cm (6-in.) Kynar Mesh demister.	507	1,521
Flocculant feeder			1	Basic "dry feeder." Nalco Part No. 201-DNF500B.88.	32,421	32,421
Clarifier			2	2 Parkson inclined plate, 5,678 L/min (1,500 gpm). 7 .62 m (25 ft) long, 3.50 m (11.5 ft) wide, 6.10 m (20 ft) high.		402,000
Sludge holding tank	60,566 L	16,000 gal	1	Vertical polyethylene tank. 4.27 m (14 ft) diameter, 4.27 m (14 ft) high.	21,000	21,000
Filter aid feeder			1	Basic "dry feeder." Nalco Part No. 201-DNF500B.88.	32,421	32,421
Pre-coat slurry feed tank	18,927 L	5,000 gal	1	Vertical polyethylene tank. 2.59 m (8.5 ft) diameter, 3.81 m (12.5 ft) high.	6,875	6,875
Vacuum pre-coat filter			1	EIMCO rotary drum vacuum filter with drum 3.05 m (10 ft) diameter and 3.05 m (10 ft) long. This will provide a cycle time of 5 to 6 hr/day.	351,106	351,106
Microfilter feed tank	105,992 L	28,000 gal	1	FRP tank - 15-minutes hydraulic residence time with 20% freeboard. 5.49 m (18 ft) diameter 4.57 m (15 ft) high.	73,150	73,150
Microfiltration system	8.18 million L/day	2.16 mgd	1	MEMCOR 5,678 L/minutes (1,500 gpm) low-pressure membrane system.	800,000	800,000
On-line hexavalent chromium analyzer	Not applicable	Not applicable	1	Automated optical spectrometer. Skalar Model OPA 2000, with manifolds to accommodate up to 6 ion-exchange trains	50,000	50,000
Dirty backwash tank	34,069 L	9,000 gal	1	Vertical polyethylene tank. 3.66 m (12 ft) diameter, 3.66 m (12 ft) high.	12,150	12,150
				Subtotal Equipment Cost, $	**2,313,882**	

gpm = gallons per minute

Table E-11. Capital Cost for Ferrous Chloride System.

Direct Costs			
Purchased Equipment Cost			
	Factor, %	**Cost, $**	
Defined equipment cost, $		2,313,882	
Scoping contingency	20	462776.4	
Subtotal Purchased Equipment Cost, $		**2,776,658**	**2,776,658**
Installation Cost Factors			
	Factor, %	**Cost, $**	
Installation	54.1	1,502,172	
Instrumentation and controls	41.4	1,149,537	
Piping	78.2	2,171,347	
Electrical	12.7	352,636	
Building ($100/sq ft)	15,225	1,522,500	
Yard improvements	11.5	319,316	
Service facilities	52.5	1,457,746	
Subtotal Installation, $		**8,475,253**	
Subtotal - Direct Plant Cost, $			**11,251,911**
Indirect Costs			
Contracting and Permitting			
	Factor, %	**Cost, $**	
Engineering and supervision	33	916,297	
Construction expenses	41	1,138,430	
Administrative and miscellaneous	20	555,332	
Contractor's overhead and profit	21	583,098	
Contingency	42	1,166,197	
Subtotal Indirect Costs, $		**4,359,354**	
Subtotal Fixed Capital Investment, $			**15,611,265**
Total Capital Investment, $			**15,611,265**

Table E-12. Operation and Maintenance Cost for Ferrous Chloride System.

	Usage Rate	Units	Unit Cost, $	Units	Annual cost, $/yr.
Chemicals					
Hydrochloric acid 35%	2,573	pound/day	$0.185	pound	$173,742
Ferrous chloride 30%	3,173	pound/day	$0.135	pound	$156,350
Sodium hydroxide 25%	3,603	pound/day	$0.135	pound	$177,538
Polyelectrolyte	20.6	pound/day	$1.10	pound	$8,287
Diatomaceous earth (pre-coat media)	212	pound/day	$0.32	pound	$24,762
Electricity					
Rotating equipment	9031	kWh/day	$0.03	kWh	$98,886
Area lighting	365	kWh/day	$0.03	kWh	$3,997
Other	150	kWh/day	$0.03	kWh	$1,643
Labor					
Shift operators	11	Full-time equivalent	75	hour	$1,716,000
Waste Disposal					
Process solids	432	ton/yr	$28	ton	$12,096
Waste Characterization					
	20	Samples/year	$1,000	per sample	$20,000
Maintenance					
Maintenance	3	% fixed capital investment			$468,338
Total Operation and Maintenance Cost, $/year					**2,861,637**