0083938

SGW-38255
Revision 0

Chromium Treatment Technology Information Exchange for Remediation of Chromium in Groundwater at the Department of Energy Hanford Site

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

FLUOR®
P.O. Box 1000
Richland, Washington

Approved for Public Release;
Further Dissemination Unlimited

RECEIVED
NOV 12 2009
EDMC

SGW-38255
Revision 0

Chromium Treatment Technology Information Exchange for Remediation of Chromium in Groundwater at the Department of Energy Hanford Site

Document Type: TI Program/Project: SGW

J. Harrington
Alexco Resource US Corp

J. Mavis
T. Simpkin
CH2M HILL, Inc.

C. Lyles
Department of Energy Pantex Plant

C. Seidel
DSWA, LLC

C. Sutton
Fluor Government Group

R. Borrego
D. Kaback
B. Wielinga
Geomatrix Consultants, Inc.

J. Rouse
MWH Americas, Inc.

E. Stine
Shaw Environmental and Infrastructure, Inc.

Date Published
July 2008

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

FLUOR
P.O. Box 1000
Richland, Washington

Approved for Public Release
Further Dissemination Unlimited

R. D. Aardal 07/09/2008
Release Approval Date

TRADEMARK DISCLAIMER

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors.

This report has been reproduced from the best available copy.

Printed in the United States of America

EXECUTIVE SUMMARY

Background

Groundwater beneath much of the Department of Energy (DOE) Hanford Site 100 Areas (100-H, 100-D, and 100-K Areas) is contaminated with hexavalent chromium [Cr(VI)], a consequence of treating reactor cooling water with sodium dichromate to prevent corrosion. Remedial systems currently in place under interim Records of Decision (ROD) to treat these plumes include several pump and treat (P&T) systems, as well as an *in situ* redox manipulation barrier in the 100-D Area. Several projects are currently underway or were completed as technology demonstrations to evaluate other innovative *in situ* treatment technologies, including *in situ* bioremediation and calcium polysulfide injection. Fluor Hanford is currently evaluating final remedial approaches to treating these plumes, including treatment of sources both in the groundwater and the vadose zone.

This Chromium Treatment Technology Exchange was initiated so that DOE-RL and Fluor Hanford staff could obtain information regarding experience with full-scale remediation of chromium-contaminated groundwater from a panel of experts to support a remedial alternatives evaluation.

The panel of experts was composed of nine scientists and engineers, primarily consultants to private industry, as well as one scientist from DOE Pantex, who is implementing chromium treatment technologies at that site. Experts in both *ex situ* and *in situ* treatment were included on the panel, as well as experts in chromium chemistry and biochemistry. The list below identifies the experts, affiliation, and presentation title.

- Dr. Bruce Wielinga, Geomatrix Consultants, Inc., Environmental Chromium Biogeochemistry
- Dr. Chad Seidel, P.E., DSWA, Chromium Treatment Research for Drinking Water Application
- Jim Mavis, P.E., CH2MHill, Reductive *Ex Situ* Treatment Technologies
- Ron Borrego, P.E., Geomatrix Consultants, Inc., *Ex Situ* Treatment Alternatives Based on Discharge Options
- Chris Lyles, DOE Pantex, Chromium Treatment of Groundwater at the DOE Pantex Plant
- Dr. Thomas Simpkin, P.E., CH2MHill, Overview of Pneumatic Injection of Zero Valent Iron for *In Situ* Chromate Reduction
- Jim Rouse, MWH Americas, Inc., *In Situ* Injection and Infiltration of Calcium Polysulfide
- Jim Harrington, Alexco Resources, *In Situ* Bioremediation

- Dr. Ernie Stine, Shaw Environmental, *In Situ* Bioremediation and Calcium Polysulfide Case Studies.

The technical information exchange meeting, held April 8-10, 2008 in Richland Washington, included 1) presentations by DOE, Fluor Hanford, and Pacific Northwest National Laboratory on Hanford activities related to chromium remediation of groundwater; 2) a field trip to the 100 Areas, 3) experts' presentations, and 4) an informal discussion.

The technical report prepared by the experts summarizes each of their presentations on remedial projects for treatment of chromium in groundwater, including some discussion of the applicability at Hanford. The report is not a consensus document, but presents individual viewpoints and experiences. The author of each section is identified at the beginning of the section. This summary, however, attempts to highlight salient points that are directly applicable to Hanford chromium treatment issues, and thus, is written as such, rather than a direct reiteration of each of the individual presentations.

Chromium Chemistry, Chromium Biogeochemistry, and Other Considerations

A number of the experts discussed chromium chemistry, chromium biogeochemistry, and other considerations that could impact remedial design at the Hanford site. 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., soluble) and less toxic, many treatment technologies are based upon reduction of the hexavalent form to the trivalent form with subsequent immobilization and detoxification. 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:

- aqueous ferrous iron (either as ferrous sulfate or chloride solution)
- solid zero-valent iron
- reduce sulfur forms (added as calcium +/or sodium polysulfide, hydrogen sulfide, sulfite, metabisulfite, or dithionite)
- microorganisms (supplied with an organic carbon substrate).

Kinetically, chemical mechanisms are believed to be much more rapid than biological. 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 4 moles of chromate, while 3 moles of calcium polysulfide in chemical reduction are required to reduce 2 moles of chromate (an efficiency difference of 6:1 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, (such as nitrate and dissolved oxygen), not simply Cr(VI), and there are numerous other factors critical to selection of amendments. Many of these factors are discussed in the following sections of the report, which were each prepared by one of the experts based upon their individual experience.

At some sites the best option may involve a combination of both chemical and biological amendments. Various amendments may also be applied in different areal locations of a plume, such as the source area vs. the distal portions of the plume, and in the vadose zone vs. the saturated zone. The preferred approach involves analysis of all the evaluation criteria for each of the alternatives under consideration. .

Previous technical reviews of treatment technologies for 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 species, such as nitrate and oxygen, which may a) require much larger quantities of treatment reagents be added, because of increased electron demand [1]or b) produce wastes that may require special handling, e.g., radioactive materials, and c) the potential for release of other naturally occurring metals, such as manganese or arsenic, because of the change in redox conditions.

When considering design of any remedial system at Hanford, one must holistically take into account 1) target contaminants for remediation, 2) chemistry of the groundwater 3) geochemistry and mineralogy of the aquifer materials, 4) chemistry of the amendments, 5) geochemical interactions of the amendments, water, and aquifer materials, including any potential by-products, 6) impacts on adjacent remedial systems, 7) physical heterogeneity of the aquifer, 8) hydrogeological conditions, and 9) risk to receptors, of including the amendment itself and also any other effect on the aquifer, such as reduction in concentrations of dissolved oxygen, 10) proximity to receptors, 11) treatment of the source of contamination (either in the groundwater or vadose zone) to ensure that contaminants do not continue to be replenished over time, 12) relative cost of capital investment and operations and maintenance, and 13) time required to achieve cleanup goals.

Because both chemical and biological mechanisms for reduction of chromate will likely follow the same chemical reaction pathway and require contact between reagent and contaminant, technology selection should be based upon other criteria, such as safety,

[1] At the in situ redox barrier in the 100-D Area, greater than 99% of the reductant is consumed by oxygen and nitrate present in the groundwater.

ease of use, by-product 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 experts favor *in situ* remedial approaches, because they claim they can be more efficient; others recognize the benefits of P&T systems for containment of the contaminant plume and removal of contaminant mass. Many of the case studies presented in the report involve sites where P&T had been operational for many years before an *in situ* treatment approach was implemented, due to lack of remedial progress with the P&T 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 experts believe that at Hanford a plume-wide *in situ* treatment approach including vadose-zone source treatment could result in cleanup within a few years using a holistic strategy, whereas P&T 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.

Ex-Situ Technologies for Treatment of Chromium in Groundwater and Potential Application at Hanford

The presentations describing experience with *ex-situ* treatment of 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 and their associated performance:

- adsorption (9 media): poor to excellent
- ion exchange (5 resins tested, regeneration vs. throw away): excellent
- 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 3 technologies as leading candidates for demonstration-scale testing (Phase III):

- Strong base anion (SBA) exchange resin
- Weak base anion (WBA) exchange resin (6 tested for Phase III Bridge Project: two outperformed the others [Resin-Tech SIR 700 and Rohm & Haas Duolite ® A7]
- Reduction/Coagulation/Filtration.

It is the opinion of Dr. Chad Seidell, the expert involved in this work, that Hanford may not be operating the existing P&T systems under optimal conditions, thus experiencing higher operational costs. Dr. Seidell believes that improvements would extend the time

between resin generation cycles and minimize waste production. Further, he recommends that on-site bench or pilot-scale testing of current market-available SBA resins and comparison to both WBA resins and reduction/coagulation/filtration should be performed to determine the best solution for specific Hanford conditions. (Note: an on-site resin testing plan has been prepared and a resin test skid has been procured for testing of performance of various resins.)

Reductive *ex situ* treatment technologies presented at the workshop include: sulfur dioxide and its derivatives (sulfite/meta-bisulfites, 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 and performance to meet cleanup standards. Polysulfide has recently been used for surface treatment of extracted groundwater prior to reinjection into the aquifer.
- Ferrous chloride or sulfate treatment is effective, inexpensive, and rapid, but generates four times the sludge mass as that of reduced sulfur compounds. Ferrous iron can be easily oxidized, and thus, must be controlled; this is easily done.
- One benefit of electrocoagulation is that it does not introduce anions into the treated water system. However, testing at Hanford demonstrated long-term operational issues with electrode passivation and cathode scaling.
- Zero-valent iron (ZVI) requires acidification of the influent groundwater prior to treatment to overcome coating with ferric hydroxide, but the acidic conditions promote dissolution of the ZVI 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.

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, cost, etc. *Ex situ* technologies described as alternatives in this section of the report include: coagulation/filtration, ion exchange, reverse osmosis, and 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 Considerations for *Ex Situ* Applications

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 reinjection of treated water after *ex situ* treatment:

- Treated water should be filtered for 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.

***In Situ* Technologies for Treatment of Chromium in Groundwater and Potential Applications at Hanford**

The two keys to successful remediation of chromium in groundwater via *in situ* methods are: 1) selection of the appropriate reductant 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 (both calcium polysulfide and zero-valent iron) has been applied to full-scale treatment of chromium in groundwater at numerous sites. These technologies can be used to treat source zones, dissolved plumes, or as a barrier using injection wells for Hanford application in the 100 Area. The amendments are delivered to the subsurface as dissolved reagents in injected fluid or solids, typically as an atomized slurry. Other *in situ* amendments have been utilized for treatment of chromium, including sodium dithionite at the Hanford Site and gaseous hydrogen sulfide for treatment of chromium in the vadose zone at the White Sands Missile Range. The most mature in situ biological and chemical reduction technologies, however, were discussed by several of the experts at the Hanford Chromium Technical Exchange and thus, are presented herein.

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 with their application lies with the actual distribution of the amendment in the subsurface, which will determine the overall success of the remediation. Further information on amendment delivery approaches is provided below in Table ES-1. This table is followed by ES-2, which describes features of the three above *in situ* treatment technologies.

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

- Will consume nitrate
- Will also consume other constituents, such as oxygen
- Can be applied to plume treatment, repair of ISRM barrier, creation of new barrier, and infiltration in source zones (e.g., source areas within the vadose zone)
- May release other naturally occurring constituents that reside in the soil matrix, such as manganese, arsenic, etc.

All three *in situ* technologies have been proven to reduce Cr(VI) in groundwater. All there technologies can be used alone or in combination.

Table ES-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 utilize existing P&T 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 down-gradient and inject up-gradient in source area	• Conversion of Hanford P&T 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 down-gradient impacts on river (may require injection of water 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, pipe grids)	• Good alternative that avoids plugging of injection wells in recirculation systems • Down-gradient 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

Table ES-2. In Situ Remediation Technologies

Technology/Amendment	Emplacement Mechanism	Design Considerations	Strengths/ Weaknesses	Cost	Performance
Bioremediation (liquid amendment) Substrates include: • Alcohols • organic acids • sugar syrups • vegetable oils • other organic wastes Each has advantages and disadvantages (see Sections 9 and 10 of the report)	Typically done on a wide injection- well spacing	• Presence of additional contaminants must be considered, as they could impact longevity of reducing capacity; others may concentrate 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 P&T systems
Reduced Sulfur Compounds (liquid amendment) • Calcium Polysulfide (liquid amendment) • Ferrous Sulfide • Sodium Metabisulfite (Other sulfur-based chemicals, such as sodium dithionite, are available)		Can combine with addition of carbon source to prevent production of excess sulfate Must consider other constituents that will utilize 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 water must be pumped and reinjected to achieve Cr(VI) 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, nitrate, and release of potential contaminants due to change in redox state • Minimum dose ≥0.5%	• Strong reductant, can be added as high dose • Exposure to oxygenated waters could produce ferric oxide coatings on ZVI particles	$4.15 to $17 per lb of ZVI emplaced	• Results from 12 sites, depths from <35-100 feet below ground surface (bgs) • ~70% good distribution • ~63% good performance • ~50% were fractured

Other Comments Regarding Hanford Design Considerations

The following are additional comments made by one or more of the experts regarding uncertainties that make the remedial evaluation and design process in the 100-D Area more challenging. These uncertainties, however, should be considered during the evaluation and design process planned for the 100-D Area.

- The source is only partially known, but must be addressed in remedial design.
- Existing plumes are not fully delineated laterally and vertically.
- Flux of water through the vadose zone is unknown and thus adds uncertainty to surface infiltration as an approach. An infiltration test could however be conducted to improve this understanding.
- Groundwater/surface-water interactions are not fully understood and can influence remedial design through re-oxidation of byproducts, seasonal impacts, longevity of reduced zones through introduction of oxygenated water, and a requirement for oxygenated water (>6 ppm) in near-river monitoring wells.
- Heterogeneity of the aquifer may impact the strength of the reduced zones and must be considered in the remedial design.
- Lower permeability units or stringers may serve as a long-term source of Cr and thus could impact remedial effectiveness and estimates of schedule requirements.
- Plumes currently impacting the river may require more immediate attention, possibly using different technologies, than those where receptor access is limited.

In summary, while optimization of the current P&T systems and/or incorporation of new treatment media may provide cost benefits, there was general consensus among the experts that treatment of the chromium plume in the 100 Area of Hanford with P&T technology alone will require many decades of treatment. To expedite the cleanup process, a more aggressive holistic approach that utilizes both *ex situ* and *in situ* technologies, while addressing both the groundwater and vadose zone, is suggested. *In situ* reduction of Cr(VI) can be readily accomplished with either chemical or biological approaches, or a combination thereof and there are a variety of potential methods for delivery of reductive amendments. Whichever approach or combination of approaches is ultimately implemented, it will be important to maintain hydraulic control to ensure protection of the Columbia River and avoid potential impacts to the current P&T systems that are emplaced to contain the plume.

TABLE OF CONTENTS

1.0 INTRODUCTION 1
- 1.1 PROBLEM 1
- 1.2 OBJECTIVE AND APPROACH 1
- 1.3 ORGANIZATION OF THE REPORT 2

2.0 ENVIRONMENTAL CHROMIUM BIOGEOCHEMISTRY AS IT RELATES TO REMEDIAL DESIGN AND PERFORMANCE 3
- 2.1 CHROMIUM REDOX CHEMISTRY 4
- 2.2 ADSORPTION/DESORPTION REACTIONS 6
- 2.3 ENHANCED *IN SITU* CR(VI) REMEDIATION 6
- 2.4 PREVIOUS TECHNICAL REVIEWS AND LESSONS LEARNED 7
- 2.5 APPLICABILITY TO HANFORD SYSTEMS-WIDE REMEDIAL STRATEGY 7
- 2.6 REFERENCES 10

3.0 CHROMIUM TREATMENT RESEARCH FOR DRINKING WATER APPLICATION 13
- 3.1 INTRODUCTION 13
- 3.2 GLENDALE CR(VI) TREATMENT PROGRAM: SUMMARY 13
  - 3.2.1 Phase I Bench-scale Studies 14
  - 3.2.2 Phase II Pilot Studies 17
  - 3.2.3 Phase III Bridge Project 19
- 3.3 RECOMMENDATIONS FOR APPLICATION AT HANFORD PUMP AND TREAT SYSTEMS 20
  - 3.3.1 Performance Optimization of Existing SBA Exchange Treatment Equipment 20
  - 3.3.2 Consider Changes to Existing SBA Exchange Treatment Equipment 20
  - 3.3.3 Consider WBA Exchange Treatment Equipment 20
  - 3.3.4 Integrate Multiple Water Quality Objectives with Treatment Selection 21
  - 3.3.5 Compare Current and Select Future Chromium Treatment Systems on a Cost Basis 21
- 3.4 REFERENCES 21

4.0 REDUCTIVE *EX SITU* TREATMENT TECHNOLOGIES 23
- 4.1 INTRODUCTION 23
- 4.2 SULFUR DIOXIDE/SULFITE/*META*BISULFITE/BISULFITE (S^{IV}) 23
  - 4.2.1 Case History 24
  - 4.2.2 Findings and Recommendations 24
- 4.3 FERROUS CHLORIDE OR SULFATE (FE^{II}) 25
  - 4.3.1 Case History 26
  - 4.3.2 Findings and Recommendations 27
- 4.4 ELECTRO-COAGULATION 28
  - 4.4.1 Case History: Hanford 100-D Area 29
  - 4.4.2 Findings and Recommendations 31
- 4.5 ZERO-VALENT IRON 33
  - 4.5.1 Findings and Recommendations 34
- 4.6 FERROUS SULFIDE 34

4.6.1 Findings and Recommendations 35
4.7 COMPARISON OF REDUCTIVE *EX SITU* TECHNOLOGIES 35
4.8 REFERENCES 36

5.0 EX-SITU TREATMENT ALTERNATIVES BASED ON DISCHARGE OPTIONS 37
5.1 STATEMENT OF PROBLEM 37
5.2 POSSIBLE DISCHARGE ALTERNATIVES 37
5.3 TREATMENT GOALS 37
5.4 AVAILABLE *EX SITU* TREATMENT TECHNOLOGIES 38
5.4.1 Brief Description of Available Treatment Technologies 39
5.4.2 Treatment Considerations 40
5.5 DISCUSSION OF DISCHARGE ALTERNATIVES 41
5.5.1 Discharge to a waterway 42
5.5.2 Municipal drinking water 42
5.5.3 Urban Green Space Irrigation 42
5.5.4 Agricultural Reuse 42
5.5.5 Industrial Reuse 42
5.5.6 Wetlands Creation or Maintenance 43
5.5.7 Aquifer Recharge 43
5.6 SUMMARY 43

6.0 CHROMIUM TREATMENT IN GROUNDWATER AT THE DOE PANTEX PLANT, AMARILLO TX 45
6.1 BACKGROUND 45
6.2 GROUNDWATER 45
6.2.1 Groundwater Impacted with Chromium 45
6.2.2 Corrective Measures Implemented for Chromium Treatment 46
6.2.3 Lessons Learned 50

7.0 OVERVIEW OF PNEUMATIC INJECTION OF ZERO VALENT IRON FOR IN-SITU CR(VI) REDUCTION 51
7.1 TECHNOLOGY OVERVIEW 51
7.2 TECHNICAL BASIS 53
7.3 STRENGTHS AND WEAKNESSES 53
7.4 OPTIMIZATION OF THE TECHNOLOGY 54
7.5 LIFE CYCLE COSTS 54
7.6 GENERAL PERFORMANCE SUMMARY 54
7.7 CASE STUDY PERFORMANCE SUMMARY 55

8.0 SUMMARY OF THE HISTORY OF *IN-SITU* REDUCTION OF HEXAVALENT CHROMIUM USING CALCIUM POLYSULFIDE 59
8.1 INTRODUCTION 59
8.2 CASE STUDY: UNIVERSAL FOREST PRODUCTS, GRANGER, INDIANA. 60
8.2.1 Site Conditions 60
8.2.2 Approach 60
8.2.3 Success 60
8.2.4 Lessons Learned 60
8.2.5 Application to Hanford 60
8.3 CASE STUDY: VALLEY WOOD PRESERVING, TURLOCK, CALIFORNIA 61

8.3.1 Site Conditions 61
8.3.2 *In Situ* Remedial Approach 61
8.3.3 Success 61
8.3.4 Lessons Learned 62
8.3.5 Application to Hanford 63
8.4 CASE STUDY: CARTER HOLT HARVEY, MOUNT GAMBIER, SOUTH AUSTRALIA ..63
8.4.1 Site Conditions 63
8.4.2 Approach 63
8.4.3 Lessons Learned 64
8.4.4 Application to Hanford 64
8.5 MARLEY COOLING TOWER COMPANY, STOCKTON, CALIFORNIA 64
8.5.1 Site Conditions 64
8.5.2 Approach 64
8.5.3 Success 66
8.5.4 Lessons Learned 66
8.5.5 Application to Hanford 66
8.6 COAST WOOD PRESERVING, UKIAH, CALIFORNIA 67
8.6.1 Site Conditions 67
8.6.2 Approach 67
8.6.3 Success 67
8.6.4 Lessons Learned 67
8.6.5 Application to Hanford 68
8.7 BOEING, LONG BEACH, CALIFORNIA 68
8.7.1 Site Conditions 68
8.7.2 Approach 68
8.7.3 Success 69
8.7.4 Lessons Learned 69
8.7.5 Application to Hanford 69
8.8 SUMMARY 69

9.0 *IN SITU* BIOREMEDIATION 72
9.1 HANFORD 100 AREA SITE-SPECIFIC ISSUES 72
9.2 COMPARISON OF *IN SITU* TREATMENT REAGENT ALTERNATIVES 73
9.2.1 Benefits 73
9.2.2 Limitations 74
9.3 PROPOSED APPROACHES 75
9.3.1 Direct Injection with Treated Water 75
9.3.2 Interaction of *In Situ* Remediation with a P&T System 76
9.3.3 Recirculation Delivery Approaches 77
9.3.4 *In Situ* Redox Manipulation Barrier Rehabilitation with Organic Carbon Recirculation Injections 78
9.3.5 Injection Through the Unsaturated Zone by Infiltration 78
9.3.6 Management of Reduced Secondary Byproducts Migration to the Columbia River 78
9.3.7 Carbon Source Selection 79
9.4 SUMMARY 80

10.0 TWO *IN SITU* REMEDIATION CASE STUDIES FOR TREATMENT OF CHROMIUM IN GROUNDWATER 81
10.1 INTRODUCTION AND CHEMISTRY 81
10.1.1 Chemistry 81
10.1.2 Remedial Concept 81
10.2 GROUNDWATER CHROMIUM TREATMENT STANDARDS 82
10.2.1 Natural Attenuation 82
10.2.2 Conventional Pump and Treat 83
10.2.3 Chemical Reduction of Cr(VI) 83
10.2.4 Biological Reduction 85
10.3 CASE STUDIES 87
10.3.1 Selma Pressure Treating Superfund Site 87
10.3.2 Ecodyne 89
10.4 TECHNOLOGY IMPLEMENTATION CONCERNS, ADVANTAGES AND DISADVANTAGES 90
10.5 CONCLUSIONS 91
10.5 REFERENCES 91

TABLES

Table 1. Comparative Performance of Investigated Technologies 16
Table 2. Technologies Evaluated in Phase II Pilot-Testing 18
Table 3. Comparison of Technologies for *Ex Situ* Reduction Cr(VI) 36
Table 4. Total Chromium Treatment Goals 38
Table 5. Summary of Performance at Field Sites 55
Table 6. Treatment Standards in the United States 82

FIGURES

Figure 1. Schematic Representation of Dominant Environmental Reactions of Chromium 3
Figure 2. Eh-pH Diagram for Chromium 5
Figure 3. Rate Comparison for Cr(VI) Reduction by Chemical and Biological Constituents 6
Figure 4. Glendale Cr(VI) Treatment Program Plan 14
Figure 5. Potential Pathways of Chromium Treatment 15
(adapted from Brandhuber et al., 2004) 15
Figure 6. Schematic Diagram of Cr(VI) Reduction Process using Sodium *meta*-Bisulfite 24
Figure 7. Schematic Diagram of Cr(VI) Reduction Process using Ferrous Iron 26
Figure 8. Cr(VI) Concentration versus Batch Reaction Time 27
Figure 9. Schematic Diagram of Electro-coagulation System Process 28
Figure 10. Electro-coagulation Cell with Plate-and-Frame Construction 29
Figure 11. Electro-coagulation Cell Voltage and Amperage during Pilot Testing 30
Figure 12. Cr(VI) Influent and Effluent during Pilot Testing 30
Figure 13. Typical Electro-coagulation Electrode Fouling 33

Figure 14. Passive Treatment of Chrome Plating Rinse Water in Packed Bed of Steel Shot 34
Figure 15. The Pantex Plant near Amarillo Texas 45
Figure 16. Chromium Concentrations in the Perched Aquifer at Pantex 46
Figure 17. Injection Well Grid for the *In Situ* Treatment Area in the Southeast Portion of the Pantex Site 48
Figure 18. Chromium Concentrations over Time during Emulsified Soybean Oil Pilot Study 49
Figure 19. *In Situ* Treatment Area Overlain on a Map of Chromium Concentrations (blue hatched lines) 49
Figure 20. Pneumatic Injection Process 52
Figure 21. Slurry Atomization 52
Figure 22. Pneumatic Injection Equipment at CNC SWMU25 56
Figure 23. Typical Pressure Response Curve (23 to 25 feet bgs) 57
Figure 24. Cr(VI) Concentrations in Well E070GW01D over Time 58
Figure 25. Variations in Chromium Concentrations over Four Sampling Periods, Valley Wood Preserving Facility 62
Figure 26. Post-Injection Chromium Concentrations Across the Pilot Study Area 65

APPENDICES

Appendix A Workshop Agenda
Appendix B Workshop Attendee List

This page intentionally left blank

TERMS

bgs	below ground surface
CCU	Cold Creek Unit
CERCLA	*Comprehensive Environmental Response, Compensation, and Liability Act of 1980*
FH	Fluor Hanford, Inc.
HEIS	Hanford Environmental Information System
HP	horsepower
ID	inside diameter
OD	outside diameter
OU	Operable Unit
RLM	Ringold Lower Mud
SGLS	Spectral Gamma Logging System
TD	total depth

This page intentionally left blank

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	0.0836	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	Millibecquerel	millibecquerel	0.027	picocuries

This page intentionally left blank

TECHNOLOGIES WORKSHOP FOR TREATMENT OF CHROMIUM IN GROUNDWATER

1.0 INTRODUCTION

1.1 PROBLEM

Groundwater beneath much of the Department of Energy (DOE) Hanford Site 100 Areas (100-H, 100-D, and 100-K Areas) is contaminated with hexavalent chromium [Cr(VI)], a consequence of treating reactor cooling water to prevent corrosion. Remedial systems currently in place under interim Records of Decision (ROD) to treat these plumes include several pump and treat (P&T) systems (100-H and 100-K Areas), as well as an *in situ* redox manipulation barrier (100-D Area). Several projects are currently underway or were completed as technology demonstrations to evaluate other innovative *in situ* treatment technologies, including *in situ* bioremediation and calcium polysulfide injection. Fluor Hanford is currently re-evaluating approaches to treating these plumes.

1.2 OBJECTIVE AND APPROACH

The purpose of this project is to convene an independent panel of experts who are currently executing remediation of chromium-contaminated groundwater, so they can provide information about this experience at such a level that Fluor can evaluate the potential applicability and desirability of employing similar treatment systems at Hanford in the 100 Area.

The panel of experts was composed of nine scientists and engineers, primarily consultants to private industry and the Department of Defense, as well as one scientist from DOE Pantex, who is implementing chromium treatment technologies at that site. Experts in both *ex situ* and *in situ* treatment were included on the panel, as well as experts in chromium chemistry and biochemistry. A list of the experts, their affiliation, and the title of their presentation follows in order that they are presented in the report:

- Dr. Bruce Wielinga, Geomatrix Consultants, Inc., Environmental Chromium Biogeochemistry
- Dr. Chad Seidel, P.E., DSWA, Chromium Treatment Research for Drinking Water Application
- Jim Mavis, P.E., CH2MHill, Reductive *Ex Situ* Treatment Technologies
- Ron Borrego, P.E., Geomatrix Consultants, Inc., *Ex Situ* Treatment Alternatives Based on Discharge Options
- Chris Lyles, DOE Pantex, Chromium Treatment of Groundwater at the DOE Pantex Plant

- Dr. Thomas Simpkin, P.E., CH2MHill, Overview of Pneumatic Injection of Zero Valent Iron for *In Situ* Chromate Reduction
- Jim Rouse, MWH Global, Inc., *In Situ* Injection of Calcium Polysulfide
- Jim Harrington, Alexco Resources, *In Situ* Bioremediation
- Ernie Stine, Shaw Environmental, *In Situ* Bioremediation and Calcium Polysulfide Case Studies.

The technical workshop was held April 8-10, 2008 in Richland Washington. The detailed workshop agenda is provided in Appendix A. On April 8, Hanford staff, including DOE, Fluor Hanford, and Pacific Northwest National Laboratory personnel, gave presentations on various activities, either completed or ongoing at Hanford, related to chromium remediation of groundwater. After the presentations, a field trip to the 100 Areas was held. On April 9, the experts' presentations were made; on April 10th an informal discussion was held. At least 50 people attended the workshop. The attendee list is provided in Appendix B.

1.3 ORGANIZATION OF THE REPORT

The remainder of the report is organized with a section for each of the expert speakers, summarizing their workshop presentation in a context based upon their learnings on the first day of the workshop, when information was presented on Hanford-specific problems, issues, and progress. The order of the sections follows the order of the presentations at the workshop. The report does not represent consensus opinion, but simply presents information from each of the experts in a separate section. As a result, there is some duplication that cannot be avoided.

During the open discussion on the last day, topics discussed included the application of horizontal wells and infiltration basins for delivery of treatment media for *in situ* treatment. There is significant discussion of the use of infiltration basins in most of the *in situ* treatment sections, e.g., Sections 8 and 9.

2.0 ENVIRONMENTAL CHROMIUM BIOGEOCHEMISTRY AS IT RELATES TO REMEDIAL DESIGN AND PERFORMANCE

By Bruce Wielinga, Ph.D., Geomatrix Consultants, Inc.

The environmental biogeochemistry of chromium in the subsurface is affected by a number of complex processes (Figure 1). Therefore, an understanding of the dominant reactions that affect each of these processes is fundamental for selecting and predicting the effectiveness of a remedial strategy. In addition, assessment of the many other reactions that are likely to occur when an amendment is introduced to the subsurface to change redox conditions can also provide useful insight into potential pitfalls and remedial effectiveness. This section reviews the dominant reactions that affect chromium speciation and other biogeochemical reactions that can impact *in situ* chromium remediation.

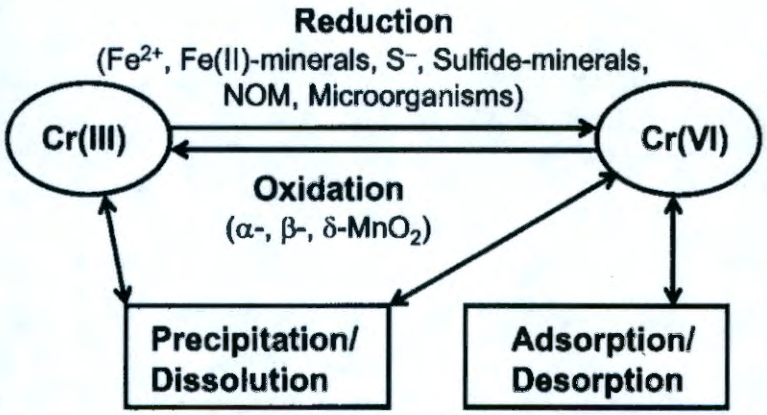


Figure 1. Schematic Representation of Dominant Environmental Reactions of Chromium
(adapted from Rai et al., 1989)

Chromium can exist in oxidation states ranging from +6 to -2, but only the +6 [hexavalent chromium, Cr(VI)] and +3 [trivalent chromium, Cr(III)] oxidation states are commonly encountered in natural environments. These species have widely contrasting toxicity and transport characteristics.

The dominant Cr(VI) species include $HCrO_4^-$ and CrO_4^{2-}, with the chromate ion (CrO_4^{2-}) the predominant species above pH 6.5. Under acidic conditions and at total chromium concentrations greater than 10 mM, $HCrO_4^-$ polymerizes to form dichromate, $Cr_2O_7^{2-}$ by the reaction 1 below:

$$HCrO_4^- + HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O \qquad [1]$$

The dominance of the Cr(VI) and dichromate ions imparts a yellow or orange color to contaminated water, respectively, at concentrations above about 1 mg/L.

In the Cr(III)-H_2O system, Cr(III) forms strong complexes with hydroxides and the dominant hydroxo species are $CrOH^{2+}$, $Cr(OH)_3^0$, and $Cr(OH)_4^-$ at pH values between 3.8 and 6.3, 6.3 to 11.5, and > 11.5, respectively (Rai et al., 1987). Under slightly acidic to alkaline conditions, Cr(III) can precipitate as an amorphous chromium hydroxide [$Cr(OH)_3$] and the solubility of $Cr(OH)_3$ keeps the chromium concentration less than the drinking water limit between pH 6 and 12 (Rai et al., 1989).

Once released to the environment, chromium is susceptible to oxidation-reduction reactions that dramatically alter its physical and chemical properties (Palmer and Puls, October 2000). Hexavalent chromium, Cr(VI), partitions weakly onto solids in soils and waters and consequently tends to be mobile in the environment. Additionally, Cr(VI) is acutely toxic (Babich et al., 1982; Beyersmann et al., 1984), subject to biological uptake (Turner and Rust, 1971), and is teratogenic and carcinogenic (Abbasi and Soni, 1984; Yassi and Nieboer, 1988). In contrast, trivalent chromium, Cr(III), has a limited hydroxide solubility and forms strong complexes with soil minerals making it relatively immobile and less available for biological uptake (Sass and Rai, 1987; Fendorf et al., 1992). Furthermore, Cr(III) is essential (at low concentrations) in human nutrition and is only slightly toxic to plants at very high concentrations.

Because of the significant differences in the physical and chemical properties of hexavalent and trivalent chromium, *in situ* methods for reducing Cr(VI) to Cr(III) are being explored as a cost-effective means to remediate chromium-contaminated sites. Therefore, understanding processes that promote the reduction of Cr(VI) to Cr(III) with the subsequent detoxification and immobilization is of considerable importance.

2.1 CHROMIUM REDOX CHEMISTRY

Chromium(VI) is a strong oxidant, as shown by its stability only under high redox potentials (Figure 2); it reacts and is reduced by numerous reducing agents commonly found in the environment, such as aqueous ferrous iron and sulfide, minerals containing ferrous iron and sulfide, natural organic matter (NOM), and microorganisms. While Cr(VI) can be reduced by biological and/or chemical means, it is often difficult to determine whether reduction is mediated principally by direct enzymatic reduction or by chemical reduction.

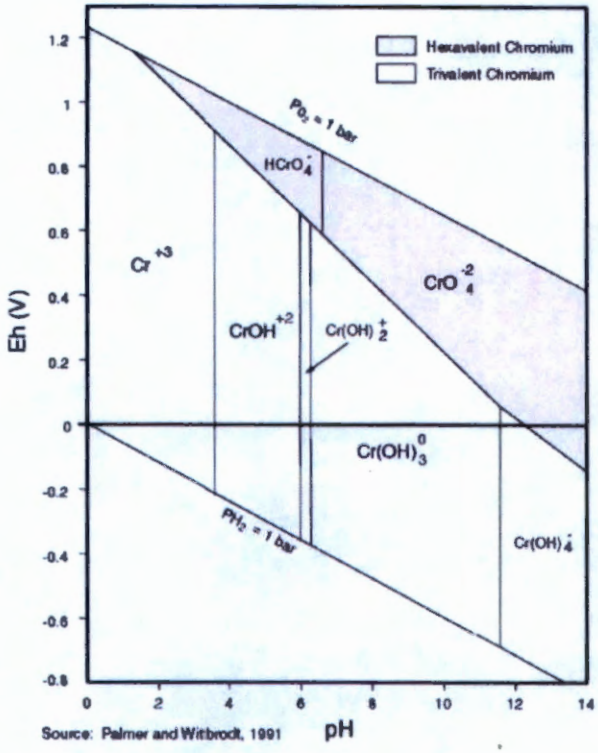


Figure 2. Eh-pH Diagram for Chromium

However, it is likely that the specific pathway by which reduction takes place will be defined by the operating reaction kinetics. Published rate expressions indicate that, of the possible chemical reductants in natural environments, ferrous iron and dissolved sulfide will dominate the reduction of Cr(VI) (Fendorf et al., 2000). By comparing reduction rates resulting from Fe(II) and S(-II) with those reported for direct microbial reduction, we can postulate operating reaction pathways. The normalization of microbial reduction rates determined under different conditions and comparison with chemical reaction rates from laboratory-derived rate expressions is admittedly tenuous. Nevertheless, by using *Desulfovibrio vulgaris* as a model Cr(VI) reducer, one notes that the chemical reduction of Cr(VI) by ferrous iron is more than 100 times faster than the observed biological rate (Figure 3). Thus, it seems likely that chemical reduction will be the major avenue by which Cr(VI) is reduced when either ferrous iron or sulfide are present (i.e., anaerobic environments). Furthermore, based on reaction kinetics, it is likely that above a pH of about 5.5, the reduction of Cr(VI) by ferrous iron would be dominant over that by sulfide.

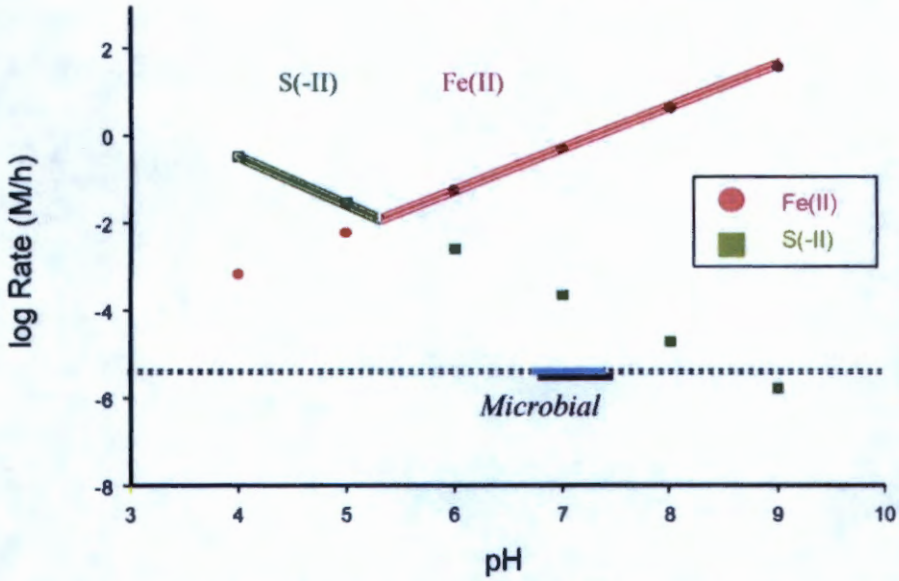


Figure 3. Rate Comparison for Cr(VI) Reduction by Chemical and Biological Constituents
(Wielinga et al., 2001)

Generation of reductant pools (e.g., Fe^{2+} and HS^-) in natural environments, however, often depends on microbial activity, because Fe(III) and sulfate reduction occurs primarily via dissimilatory bacterial reduction pathways (Lovley, 1991; Lovley et al., 1991). This brief review indicates that reduction of chromium in soils and groundwater occurs through complex interactions of synergistic and competing chemical and biological processes. In the following sections many of these reactions are described.

2.2 ADSORPTION/DESORPTION REACTIONS

Most Cr(VI) solid phases are expected to be relatively soluble under environmental conditions, and hence, in the absence of solubility controlling solids, the aqueous concentration of Cr(VI) under acidic to slightly alkaline conditions will be primarily controlled by adsorption/desorption reactions (Rai et al., 1989). Chromium(VI) is adsorbed by iron and aluminum oxides, kaolinite, and to a lesser extent montmorillonite (Rai et al., 1989). At higher concentrations, there is little retardation of Cr(VI), thus chromate removal/reduction via P&T systems can be efficient. However, as the concentration decreases, it becomes progressively more difficult to remove chromium mass (Palmer and Wittbrodt, 1991). Cr(VI) adsorption/desorption reactions are likely a significant factor in the very long time frames required for P&T remediation to reduce Cr(VI) concentrations to below the maximum contaminant level (MCL).

2.3 ENHANCED *IN SITU* CR(VI) REMEDIATION

At sites where the subsurface is enriched in natural reductants and/or with a long pathway to potential receptors, natural attenuation of Cr(VI) is a possible remedial option. At sites where

these conditions are not met, various reductants can be added to the subsurface to enhance Cr(VI) reduction. Common reductants used for *in situ* Cr(VI) reduction include:

- reduced sulfur compounds – calcium polysulfide (CaS_x), sulfite (HSO_3^-), sulfide (H_2S), and dithionite ($S_2O_4^{2-}$);
- reduced iron compounds – ferrous sulfate, ferrous chloride, zero-valent iron (ZVI); and
- organic compounds to enhance microbial activity for bioremediation.

Careful selection of a reductant and a delivery method are crucial components for achieving a successful and cost-effective remedial program, given site specific hydrologic and geochemical conditions.

2.4 PREVIOUS TECHNICAL REVIEWS AND LESSONS LEARNED

In early 2004, DOE Richland and Fluor Hanford requested technical assistance from the DOE Headquarters EM-23 Technical Assistance Program to provide a team of technical experts to evaluate potential causes for the decreasing effectiveness of the *In Situ* Redox Manipulation (ISRM) Barrier installed between 1999 and 2003 in the 100-D Area. In late 2004, a second request for assistance was made to the DOE Headquarters EM-23 Technical Assistance Program for a team of experts to develop recommendations for mending the ISRM barrier in the 100-D Area of the Hanford Site.

The most relevant findings from the two technical assistance panels convened in 2004 are briefly summarized below.

The most probable causes for Cr(VI) breakthrough in the barrier injection wells were:

- physical and chemical heterogeneity within the aquifer; and
- presence of other oxidants, such as nitrate, which were not recognized in the earliest predictions of barrier longevity.

A number of technologies, including *in situ* bioremediation, CaS_x and ZVI, were recommended for further consideration for mending of the ISRM barrier and/or treatment of chromium in Hanford groundwater.

2.5 APPLICABILITY TO HANFORD SYSTEMS-WIDE REMEDIAL STRATEGY

The implementation of a successful and cost-effective systems-wide remedial program to treat chromium-impacted soils and groundwater will require not only an understanding environmental chromium chemistry, but also must consider:

- geochemistry of the amendments

- probable reaction pathways
- reaction stoichiometry
- geochemistry of non-target geochemical constituents
- potential impact on other remedial systems (*i.e.* in-place P&T systems), and
- geochemistry of any residual reaction by-products.

Any technological approach will be affected by the local hydrological and geochemical heterogeneity. In previous technical assistance workshops, two potential amendments were recommended if a more active remedial approach were implemented in the 100-D Area to treat the chromium plume: CaS_x and organic compounds to promote bioremediation. The applicability of CaS_x and organic amendments is discussed further below in relation to the above criteria.

The reaction describing the reduction of Cr(VI) by CaS_x and microbial reduction with an organic carbon source are shown in equations 3 and 4, respectively (organic carbon as lactate ($C_3H_6O_3$) or as generic carbohydrate (CH_2O).

$$2CrO_4^{2-} + 3CaS_5 + 10H^+ \rightarrow 2Cr(OH)_3 + 15S^0 + 3Ca^+ + H_2O \quad [3]$$

$$C_3H_6O_3 + 4CrO_4^{2-} + 8H^+ \rightarrow 3CO_2 + 4Cr(OH)_3 + H_2O \quad [4]$$

Equations 3 and 4 provide for the assessment of reaction stoichiometry and show residual reaction products introduced to the environment. Reaction 3 shows that 3 moles of CaS_x are required to reduce 2 moles of Cr(VI), while 1 mole of lactate is required to reduce 4 moles of Cr(VI) (Equation 4). In addition, 7.5 moles of sulfur (240 g) and 1.5 moles calcium (60 g) will be deposited per mole of Cr(VI) reduced by CaS_5, while the organic compound is oxidized to carbon dioxide (CO_2).

Other potential reactions consequential to Cr(VI) reduction that are likely to occur in the subsurface when these amendments are added are shown in equations 5 through 8.

$$HS^- + 8FeOOH + 15H^+ \rightarrow 8Fe^{2+} + SO_4^{2-} + 12H_2O \quad [5]$$

$$HS^- + 2FeOOH + 5H^+ \rightarrow 2Fe^{2+} + S^0_{(s)} + 2H_2O \quad [6]$$

$$C_3H_6O_3 + 12FeOOH + 24H^+ \rightarrow 12Fe^{2+} + 3CO_2 + 21H_2O \quad [7]$$

$$2CH_2O + SO_4^{2-} \rightarrow HS^-_{(aq)} + 2HCO_3^- + H^+ \quad [8]$$

$$3Fe^{2+} + CrO_4^{2-} + 8H_2O \rightarrow 4Fe_{0.75}Cr_{0.25}(OH)_3 + 5H^+ \quad [9]$$

Equations 5 through 8 indicate that with either the chemical reductant (CaS_5) or a biostimulant (organic carbon solution) a portion of the reductant will be consumed by reduction of solid-phase iron minerals, which will indirectly reduce Cr(VI) to give the more stable $(Cr,Fe)(OH)_3$

solid solution. In fact, given the reaction rates (Figure 3) of the various potential reductants and the knowledge that >99 % of the Cr(VI) reducing capacity will come from the solid phase and that <1 % is attributed to aqueous species (Barcelona and Helm, 1991; Palmer and Puls, 1994), it is likely that the indirect reduction of Cr(VI) by reduced iron will be the dominant reaction pathway under either remedial approach. It is likely that the recirculation of Cr(VI)-laden water through the ferrous iron-rich vadose zone and aquifer materials will account for most of the Cr(VI) removal. Recent work has demonstrated the microbial reduction and cycling of iron initially precipitated in the $(Cr,Fe)(OH)_3$ solid solution (Hansel et al., 2003), thus providing a mechanism to extend Cr(VI) reduction in zones where iron concentrations may be limiting, as has been observed at Hanford.

In addition to the primary reactions directly consequential to Cr(VI) reduction and remediation, other reactions with non-target constituents will occur. These secondary reactions can be of importance, because they can consume reducing equivalents, and thereby escalate costs, and can potentially mobilize other elements, which could be cause for concern. Secondary reactions likely to occur are summarized below.

$$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+ \quad [10]$$

$$5HS^- + 8NO_3^- + 3H^+ \rightarrow 5SO_4^{2-} + 4N_{2(g)} + 4H_2O \quad [11]$$

$$CH_2O + O_{2\,(g)} \rightarrow HCO_3^- + H^+ \quad [12]$$

$$5CH_2O + 4NO_3^- \rightarrow 2N_{2(g)} + 5HCO_3^- + H^+ + 2H_2O \quad [13]$$

Equations 10 through 13 indicate that a significant amount of either possible reductant will be consumed by reaction with the non-target constituents oxygen and nitrate. Previous technical review panels have calculated that based on Hanford groundwater chemistry, greater than 99% of the reductant will be consumed by reduction of the combined oxygen and nitrate load (DOE, 2004a). The likely similar reaction pathways for calcium polysulfide and organic biostimulant along with the significant concentration of non-target oxidants, suggests that a cost-benefit analysis is appropriate in the selection of a reducing agent for Cr(VI) remediation at the Hanford site.

$$HS^-_{(aq)} + 4MnO_2 + 7H^+ \rightarrow SO_4^{2-} + 4Mn^{2+} + 4\,H_2O \quad [14]$$

$$2CH_2O + 2MnO_{2\,(s)} + 3H^+ \rightarrow 2Mn^{2+}_{(aq)} + 2HCO_3^- + 2H_2O \quad [15]$$

$$Mn^{2+} + HCO_3^- \rightarrow MnCO_{3\,(s)} + H^+ \quad [16]$$

$$2Mn^{2+} + O_2 + 2H_2O \rightarrow 2MnO_2 + 4H^+ \quad [17]$$

$$2S^0_{(s)} + 3O_2 + 2H_2O \rightarrow 2SO_4^{2-} + 4H^+ \quad [18]$$

Equations 14 and 15 demonstrate the reductive dissolution of manganese oxide under reducing conditions. While there are likely to be numerous elements released due to the dissolution of iron hydroxides, they are typically removed rapidly via adsorption on down-gradient and/or re-precipitated iron oxyhydroxides. However, manganese due to its abundance in the earth's crust can often reach fairly high concentrations under imposed reducing conditions. Equations 16

and 17 illustrate the reactions that can impose some solubility control on the concentration of manganese, however, while these phases are often predicted based on thermodynamic equilibrium, in practice slow reaction kinetics often allows the concentration of manganese to remain elevated. Thus, given the proximity of the Cr(VI) plume to the Columbia River and water treatment facilities, maintaining hydraulic control of treated water and careful monitoring of manganese is advisable. Of course, monitoring for oxygen will also be required because of the ROD amendment that requires oxygen concentrations in near-river monitoring wells to be greater than 6 ppm.

Equation 18 illustrates the oxidation of elemental sulfur as would be expected as conditions in the unsaturated zone and aquifer return to aerobic/oxidizing following treatment. The deposition of residual sulfur (potentially 240 g per mole of Cr(VI) reduced) provides a long-term source term for sulfate loading and soil/groundwater acidification.

In summary, based on our current knowledge of subsurface biogeochemistry and chromium redox chemistry, it is likely that irrespective of which amendment s selected for remediation of the Cr(VI) plume at Hanford, the same reaction pathway will dominate Cr(VI) removal. Thus other factors, such as, safety/ease of use, by-product production, and cost might help guide the selection of the most cost-effective and practicable alternative. An evaluation of these and other criteria for several possible remedial alternatives was provided in one of the earlier technical assistance reports (DOE, 2004b). From the above discussion, it is clear that addition of the chemical reductant CaS_x will result in the deposition of a considerable mass of elemental sulfur and calcium in the unsaturated zone and aquifer. In contrast, organic addition to promote bioremediation will add only additional alkalinity and CO_2. Previously generated cost estimates (DOE, 2004b) indicated that the cost for groundwater treatment using CaS_x at Hanford would range from $400 to $1,200 per kg chromium reduced, dependent on assumptions used, compared to a cost that ranged from $15 to $270 per kg chromium for an organic substrate with the same assumptions.

2.6 REFERENCES

Abbasi, S.A., Soni R., 1984. Teratogenic effects of chromium(VI) in the environment as evidenced by the impact on larvae of Amphibian Rana Tigrina : Implications in the Environmental-Management of Chromium. Int. J. Environ. Stud. 23:131-137.

Babich, H., Schiffenbauer, M., Stotzky, G., 1982. Comparative toxicity of trivalent and hexavalent chromium to fungi. Bull. of Environ. Contam. Toxicol. 28:452-459.

Barcelona, M.J., and Helm, T.R., 1991. Oxidation-reduction capacities of aquifer solids. Environ. Sci. Technol. 25:1565-1572.

Beyersmann, D., Koster, A., Buttner, B., Flessel, P., 1984. Model reactions of chromium compounds with mammalian and bacterial-cells. Toxicol. Environ. Chem. 8:279-286.

DOE, 2004a. Mending the *in situ* redox manipulation barrier. DOE Technical Solutions Report, Prepared by Concurrent Technologies Corporation, May.

DOE 2004b. Evaluation of amendments for mending the ISRM barrier. DOE Technical Solutions Report, Prepared by Concurrent Technologies Corporation, November.

Fendorf, S., Wielinga, B.W., Hansel, C.M., 2000. Chromium transformations in natural environments: The role of biological and abiological processes in chromium(VI) reduction. Int. Geol.Rev. 42: 691-701.

Fendorf, S.E., Fendorf, M., Sparks, D.L., Gronsky, R., 1992. Inhibitory mechanisms of Cr(III) oxidation by Delta-MnO_2. J. Colloid and Interface Sci. 153:37-54.

Hansel, C.M., Wielinga, B.W., and Fendorf, S., 2003. Structural and compositional evoluation of Cr/Fe solids after indirect chromate reduction by dissimilatory iron-reducing bacteria. Geochim.et Cosmo. Acta 67: 3: 401-412.

Lovley, D.R., 1991. Dissimilatory Fe(III) and Mn(IV) reduction. Microbiol. Rev. 55:259-287.

Lovley, D.R., Phillips, E.J.P., Lonergan, D.J., 1991. Enzymatic versus non-enzymatic mechanisms for Fe(III) reduction in aquatic sediments. Environ. Sci. Technol. 25:1062-1067.

Palmer, C.D. and Wittbrodt, P.R., 1991. Processes affecting the remediation of chromium-contaminated sites. Environmental Health Perspectives 92:25-40.

Palmer, C.D. and Puls, R.W., 1994. Natural attenuation of hexavalent chromium in groundwater and soils. U.S. Environmental Protection Agency, EPA Groundwater Issue, EPA/540/5-94/505.

Palmer, C.D., and Puls, R.W., 2000. *In situ* treatment of soil and groundwater contaminated with chromium: Technical resource guide. U.S. Environmental Protection Agency, EPA/625/R-00/005.

Rai, D., Sass, B.M., and Moore, D.A., 1987. Chromium (III) hydroxide donstants and solubility of chromium (III) hydroxide. Inorg. Chem. 26: 345-349.

Rai, D., Eary, L.E., Zachara, J.M., 1989. Environmental chemistry of chromium. Sci. Total Environ. 86 (1-2): 15-23.

Sass, B.M. and Rai, D., 1987. Solubility of amorphous chromium(III)-iron(III) hydroxide solid-solutions. Inorg. Chem. 26:2228-2232.

Turner, M.A. and Rust, R.H., 1971. Effects of chromium on growth and mineral nutrition of soybeans. Soil Sci. Soc. Am. Proc. 35:755-758.

Yassi, A. and Nieboer, E., 1988. Carcinogenicity of chromium compounds. In Nriagu JO, Nieboer E., eds.: "Chromium in the Natural and Human Environments." New York: Wiley and Sons, pp 443-496.

This page intentionally left blank

3.0 CHROMIUM TREATMENT RESEARCH FOR DRINKING WATER APPLICATION

By Chad Seidel, Ph.D., P.E., Damon S. Williams Associates, LLC

3.1 INTRODUCTION

Chromium (Cr) is an inorganic contaminant of concern to the drinking water industry. It exists in drinking water sources in predominantly two oxidation states: trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)]. The federal regulatory MCL for total chromium (Cr(III) + Cr(VI)]) is 100 μg/L, whereas the MCL in California set by CA Department of Public Health (DPH) is 50 μg/L. Cr(VI) has received significant public attention, much of which can be attributed to the movie *Erin Brockovich*. A more stringent Cr(VI)-specific drinking water regulation is to be developed in California.

One challenge faced by the drinking water industry in dealing with chromium was the limited experience in chromium treatment technologies. While various technologies have been applied in industrial treatment and hazardous waste management, chromium concentrations in those applications were usually 10 to 1,000 times higher than those of drinking water concern. Previous studies had not demonstrated treatment technologies to reliably reduce Cr(VI) in drinking water to concentrations to <10 μg/L. Also, there was limited knowledge on the nature of chromium treatment residuals, which further hindered the application of those technologies in drinking water applications.

The California cities of Glendale, along with Burbank, Los Angeles, and San Fernando, commissioned a study to develop treatment technologies capable of removing chromium to single microgram per liter concentrations. This section of the report provides a summary of the chromium treatment research effort in the drinking water industry. Recommendations for the chromium remediation efforts at the Hanford Site are then made based on the lessons learned and the conclusions drawn from the drinking water research.

3.2 GLENDALE CR(VI) TREATMENT PROGRAM: SUMMARY

The Glendale Cr(VI) treatment research program is described in Figure 4. This four-phase program includes (1) a bench-scale study that improved the understanding of fundamental chromium chemistry and screened promising treatment technologies, (2) a pilot-scale study that evaluated treatment technologies for removing Cr(VI) to low concentrations in Glendale groundwater, (3) a demonstration-scale study to finalize the technology evaluation and address additional costs and residual issues, and (4) full-scale implementation of an effective Cr(VI) technology. It is important to note that Phase III also involved a "bridge" project (not shown in Figure 4) that addressed some issues raised from the Phase II pilot study prior to the demonstration-scale study as described subsequently. The participants involved in each phase are listed in the figure. This section discusses the completed research efforts, which include Phase I, Phase II, and the Phase III Bridge Project. To date, two technical reports and two peer-revewed technical journal papers have been published as listed below:

- Brandhuber, P et al., 2004.

- Qin, G et al., 2005.
- McGuire, M.et al., 2006.
- McGuire, M et al., 2007.

The readers are encouraged to refer to these references for the complete details of this study.

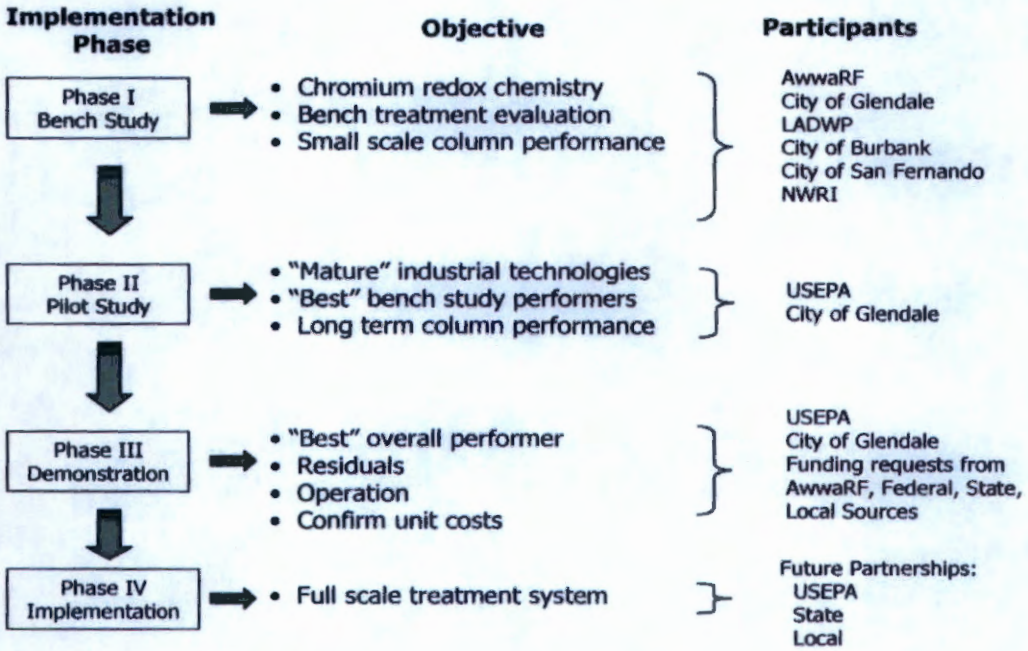


Figure 4. Glendale Cr(VI) Treatment Program Plan

3.2.1 Phase I Bench-scale Studies

This phase of the study, as summarized in Figure 5, investigated nearly all of the potential methods for controlling Cr(VI) either directly (adsorption, anion exchange, membrane filtration, electro-coagulation) or those that remove the reduced form of Cr(III) (precipitation with membranes or coagulation and precipitation with conventional or membrane filters). These technologies were investigated using laboratory-scale testing methods, including batch isotherm tests, bench membrane systems, flow-through mini-columns, and jar testing techniques. For information including raw water quality parameters and detailed experimental procedures refer to Brandhuber et al. (2004).

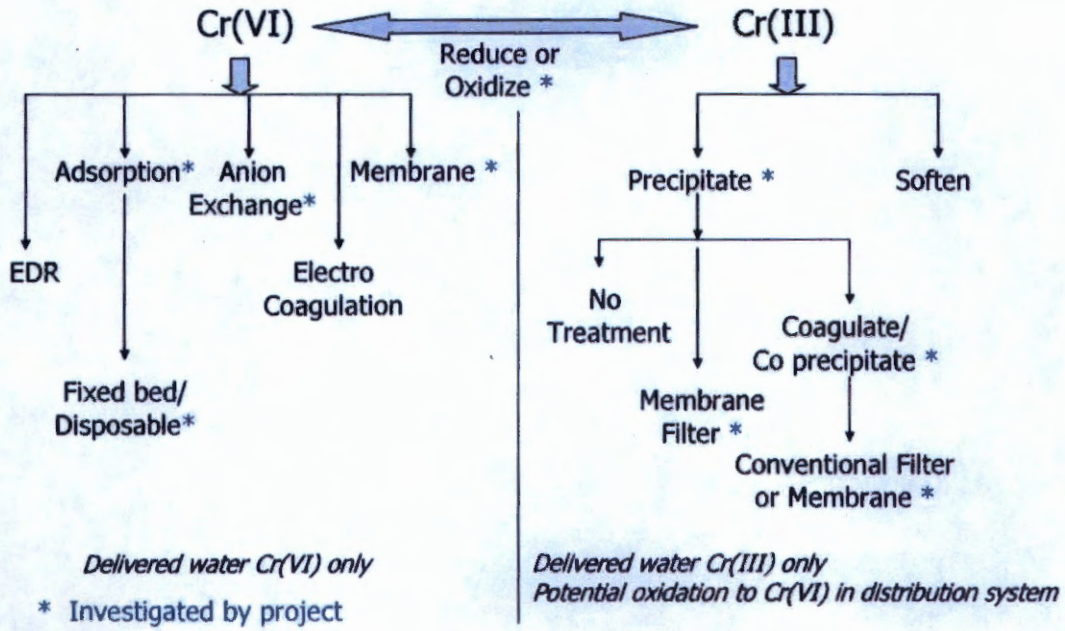


Figure 5. Potential Pathways of Chromium Treatment
(adapted from Brandhuber et al., 2004)

The performances of selected technologies evaluated in this study are summarized in Table 1. For detailed discussions on the experimental results, refer to Brandhuber et al. (2004). Their performances were designated as Excellent, Good, and Poor. Excellent refers to >90% Cr removal, whereas Good and Poor refers to 50%-90% and <50% removal, respectively. Based on their performances, anion exchange, sulfur-modified iron media, membrane treatment with nanofiltration or reverse osmosis, and coagulation and precipitation of reduced Cr(III) were recommended for Phase II pilot studies.

Table 1. Comparative Performance of Investigated Technologies
(adapted from Brandhuber et al., 2004)

Media/Membrane Type	Technology Description	Cr(VI) Treatment Performance*
	Sorption and Chelation Media	
GFH	Granular ferric hydroxide	Poor to good
Bayoxide E33	Granular ferric oxide	Poor
Sulfur-modified iron	Sulfur-modified iron	Excellent
Alcan AA-400	Activated alumina	Poor
Alcan AA-F550	Iron-coated activated alumina	Good
WTR Z24	Iron-impregnated zeolite	Good
ADI-G2	Iron oxide–coated diatomite	Poor
Vintec Bauxsol	Bauxite clay	Poor
Metre General Octolig	Metal-binding ligand	Good
	Anion Exchange Resins	
Orica MIEX®	Magnetic anion exchange	Excellent
Rohm & Haas Amberlite IRA410	Strong base type II	Excellent
DOWEX Marathon MSA	Strong base type I	Excellent
Purolite A-600	Strong base type I	Excellent
Purolite A-300	Strong base type II	Excellent
	Membranes	
GM	Ultrafilter	Poor
MX07	Nanofilter	Excellent
LFC-1	Reverse osmosis	Excellent
	Reduction and Precipitation	
Ferrous sulfate coagulant	Cr(VI) reduction to Cr(III) with precipitation and filtration with and without coagulant aid polymer	Good

* Cr(VI) Treatment Performance
- Excellent = >90% removal
- Good = 50%–90% removal
- Poor = <50% removal

The critical issues arisen from the bench study for each technology include the following:

3.2.1.1 Anion Exchange

The effect of regeneration on anion exchange performance is critical to understand. Also, the possibility of operating anion exchange on a "throw-away" basis should be evaluated.

3.2.1.2 Sulfur-modified Iron Media

The mechanisms of Cr(VI) control by sulfur-modified iron - Cr(VI) sorption or Cr(VI) reduction to Cr(III) with removal by the iron precipitates needs to be better understood. Post-treatment requirements for iron control also need to be investigated.

3.2.1.3 Membrane Treatment by Nanofiltration and Reverse Osmosis

Rejection of Cr(VI) by membrane technologies is excellent, but the operational conditions (productivity, fouling, membrane life) that affect the feasibility of this technology may require

further investigation. Because of large loss of water associated with high-pressure membrane technologies, membrane treatment is not carried forward to pilot-scale studies.

3.2.1.4 Coagulation and Precipitation of Reduced Cr(III)

This process may be capable of achieving reasonably low concentrations of chromium in treated water. Further study of mixing conditions and process kinetics is required to optimize this process for reducing Cr(VI) to very low concentrations.

3.2.2 Phase II Pilot Studies

The pilot testing was performed in the City of Glendale, CA. It was further divided into two phases: Phase A and Phase B. Phase A involved the evaluation of vendor-supplied treatment technologies, which included ion exchange with both strong base anion (SBA) and weak base anion (WBA) resins, granular activated carbon (GAC) and zeolite adsorption, magnetized ion exchange (MIEX) resin, and reduction/filtration. Phase B involved the testing of (Phase I) bench-scale proven technologies, most notably reduction/coagulation/filtration (RCF), as well as additional investigation of promising vendor systems including the performance of SBA with regeneration. The technologies examined in both Phases A and B are summarized in Table 2. The raw groundwater was obtained from the Glendale Water Treatment Plant, which was spiked with additional Cr(VI) to 100 μg/L. The treatment goal was to decrease Cr(VI) to below 5 μg/L, or 95% Cr(VI) removal. For detailed information related to this study, such as raw water quality parameters, testing conditions as well as detailed experimental results, refer to McGuire et al. (2006) and Qin et al. (2005).

Table 2. Technologies Evaluated in Phase II Pilot-Testing

Vendor	Product	Technology
US Filter/ Rohm & Haas	SBA & WBA Resins	Anion Exchange
Calgon	SBA & iron-impregnated GAC	Anion Exchange and Adsorption
Orica	MIEX®	Continuous flow reactor anion exchange
WRT® (Water Remediation Technology)	Z-24™	Surface reduction/adsorption
Filtronics	Electromedia ®	Reduction/precipitation
US Filter/Rohm & Haas	SBA Resin	Anion Exchange with Regeneration
---	--	Reduction/Coagulation/Filtration

Overall, Phase A pilot testing indicated that anion exchange technologies performed well for Cr(VI) removal. SBA resins in lead-lag column configuration were effective, but would have to be regenerated every ~2,000 bed volumes. The ability to effectively regenerate SBA resins and return them to service still needed to be determined. MIEX resin might be effective at high resin dosages. WBA resin with pH adjustment could be operated for many more bed volume before breakthrough; however; pH control issues needed to be resolved.

It was also found that the need for a frequent media replacement rendered Calgon carbon-based technologies and WRT adsorptive media economically questionable. The demonstration of reduction with precipitation performance by Filtronics was not successful. This was due to the fact that the vendor was not able to successfully operate their pilot system in the time that they were on-site.

Phase B pilot testing indicated that SBA exchange resins could be effectively regenerated and returned to capacity using a saturated brine, and accumulated sulfate and Cr(VI) ions did not appear to affect regeneration in the first regeneration cycles. Also, reduction/coagulation/filtration (RCF) was found to be much more effect at pilot-scale testing than bench-scale testing. Briefly, with doses of 25:1 and 50:1 Fe:Cr, Cr(VI) reduction to Cr(III) and subsequent filtration of Cr(III) and Fe were highly effective. There was also not a need for pH adjustment. The ability to run the system for extended periods of time made this technology viable.

In conclusion, the pilot testing identified three technologies as leading candidates for the next phase (Phase III) of demonstration-scale treatment: SBA exchange; WBA exchange, and RCF. The critical issues for each technology will be discussed in the following section.

3.2.2.1 Strong Base Anion Exchange Resin

SBA exchange is a proven technology with a history in drinking water treatment. The study showed that it was effective for up to 1,700 bed volumes. It was regenerable numerous times with recycled saturated brine solution; however; decreased treatment capacity with subsequent regenerations was observed. It was also observed that concentrated Cr(VI) was only partially removed from brine with ferrous sulfate using an established procedure, and therefore, more research is needed to achieve optimal treatment of Cr(VI) waste brine. In addition, chromatographic peaking of anions such as nitrate may present a challenge for water treatment, as shown in this pilot study.

3.2.2.2 Week Base Anion Exchange Resin

The pilot tests showed that WBA exchange was effective for Cr(VI) treatment for greater than 38,000 bed volumes; however, limited research indicated that this resin might not be regenerable. Spent media, which might contain up to 3.2 percent Cr by weight, was determined to be hazardous by the California (CA) whole effluent toxicity (WET) test, but non-hazardous by the toxic characteristic leaching procedure (TCLP). The Duolite® A7 resin is a new application to drinking water treatment.

3.2.2.3 Reduction/Coagulation/Filtration

RCF is currently an industrial process with similarities to the conventional drinking water treatment process. The pilot study showed that it was effective with daily backwashing. Unlike bench scale work, Cr(VI) reduction was independent in the range of 6.5-7.5, yet, most effective particulate removal was achieved with pH below 7.5. Complete filter cleaning could be achieved with minimal backwashing. Backwash solids could be rapidly settled with a non-ionic high molecular weight polymer dose of 1 mg/L within 2.5 minutes, that is, an overflow rate of 1 gallon per minute per square foot (gpm/ft^2). Backwash water was non-hazardous for Cr(VI), that is, <8 μg/L, after polymer addition and 20 minutes of settling. The backwash solids were classified as hazardous by the CA WET test but non-hazardous by the TCLP.

3.2.3 Phase III Bridge Project

As discussed previously, the purpose of the bridge project was to answer the questions arisen from Phase II pilot testing, most notably those around WBA exchange, which showed unexpectedly high Cr removal, but had never been tested at demonstration-scale. Specifically, the key objectives of the Phase III Bridge Project included evaluating the effectiveness of the WBA exchange resin using continuous pH adjustment, and developing better cost estimates of WBA resin. This section provides the major findings obtained from this phase. For information such as raw water quality parameters, test conditions and experimental results, and detailed cost analysis, refer to McGuire et al. (2007).

Overall six WBA resins were evaluated, and it was found that two of them outperformed the others. Resin-Tech SIR-700 and Rohm & Haas Duolite® A7 could operate for over 100,000 BVs and about 45,000 BVs, respectively, before Cr(VI) breakthrough. Cr(VI) removal was more effective at depressed pH of 6 than at pH of 6.8. Also, similar to Phase II, the spent resin passed the TCLP, but failed the CA WET test. The mechanism of Cr(VI) removal was also

investigated, where the reduction of Cr(IV) to Cr(III) was clearly identified as one of the steps for both resins.

The capital, operation and maintenance (O&M), and annualized costs were estimated for 500 gpm and 100 gpm treatments using SBA, WBA and RCF. SBA offered the lowest annualized costs, but there were uncertainties about brine disposal. RCF offered lower annualized cost than WBA, but had the highest capital cost.

The next step in this project is to select demonstration-scale technologies with the overall costs as one deciding factor.

3.3 RECOMMENDATIONS FOR APPLICATION AT HANFORD PUMP AND TREAT SYSTEMS

The research results from the drinking water community can be directly applied at the Hanford Site to the existing and potential future P&T systems, and to a lesser extent to the *in situ* remediation applications. The following section makes recommendations for application of the drinking water chromium treatment research at the Hanford Site.

The existing P&T systems operating at Hanford include on-site regenerated SBA exchange at the 100-D Area and off-site regenerated SBA exchange at the 100-H and 100-K Areas. These SBA exchange treatment systems range in size from 50 to 600 gpm. While these treatment systems are relatively small compared with those considered for municipal drinking water treatment, the research previously described is still applicable. Based on the limited information provided about the operational conditions and performance of SBA exchange systems, the following recommendations are made:

3.3.1 Performance Optimization of Existing SBA Exchange Treatment Equipment

According to the limited information provided about the operational conditions and performance of the SBA exchange systems, the Hanford systems may not be operating under optimal conditions, resulting in more expensive treatment costs. The current operational conditions (e.g., pH adjustment, regenerant brine strength, use of sacrificial lead vessel resins to address radionuclides) should be optimized to extend the time between resin regeneration cycles and minimize waste production.

3.3.2 Consider Changes to Existing SBA Exchange Treatment Equipment

The research conducted within the drinking water community indicated differences in chromium treatment performance among SBA resins. Resin selection is an important aspect of optimizing SBA exchange systems. On-site bench- or pilot-scale testing of current market available SBA resins should be conducted to determine the most efficient SBA resin for Hanford-specific groundwater quality conditions.

3.3.3 Consider WBA Exchange Treatment Equipment

As described previously, research conducted within the drinking water community indicated that WBA exchange resins can operate much longer than SBA exchange resins and would be

replaced and disposed rather than regenerated. As with SBA exchange, on-site bench- or pilot-scale testing of current market available WBA resins (e.g. Rohm & Haas Duolite A7 and ResinTech SIR-700) should be conducted to determine if WBA exchange resins offer a cost-competitive advantage over SBA exchange resins given the Hanford groundwater quality conditions. WBA exchange could potentially be implemented at the current off-site regenerated SBA exchange treatment systems at the 100-H and 100-K Areas with similar or less demanding operational requirements.

3.3.4 Integrate Multiple Water Quality Objectives with Treatment Selection

Groundwater quality at the Hanford P&T facilities varies considerably with the occurrence of chromium and several other contaminants, including nitrate and radionuclides. Treatment technology selections should integrate multiple water quality objectives to accomplish as much remediation as possible (where desired) with a given treatment system.

3.3.5 Compare Current and Select Future Chromium Treatment Systems on a Cost Basis

Several *ex situ* chromium treatment methods (e.g. SBA exchange, WBA exchange, and reduction/coagulation/filtration) have been demonstrated in previous research efforts and could be implemented at Hanford. Comparison of current and selection of future chromium treatment systems should be made on a cost basis considering capital, annual operation and maintenance, and lifecycle costs.

3.4 REFERENCES

Brandhuber, P., Frey, M., McGuire, M.J., Chao, P., Seidel, C., Amy, G., Yoon, J., McNeill, L., and Banerjee, K., 2004. Low-level hexavalent chromium treatment options: Bench-Scale Evaluation: AWWARF, Denver, CO.

McGuire, M.J., Blute, N.K., Seidel, C., Qin, G., and Fong, L., 2006. Pilot-scale studies of hexavalent chromium removal from drinking water. Journal AWWA, 98(2):134-143.

McGuire, M.J., Blute, N.K., Qin, G., Kavounas, P., Froelich, D., and Fong, L., 2007. Hexavalent chromium removal using anion exchange and reduction with coagulation and filtration: AWWARF and the City of Glendale Water and Power, Denver, CO.

Qin, G., McGuire, M.J., Blute, N.K., Seidel, C., and Fong, L., 2005. Hexavalent chromium removal by reduction with ferrous sulfate, coagulation, and filtration: A pilot-scale study. Environ. Sci. Technol. 39(16):6312-6327.

This page intentionally left blank

4.0 REDUCTIVE *EX SITU* TREATMENT TECHNOLOGIES

By Jim Mavis, P.E., CH2M HILL, Inc.

4.1 INTRODUCTION

A variety of Cr(VI) reduction processes have been used in industry for many years. Some of them are no longer in use and others have features that make them well suited for use only in specific applications.

Five of these *ex situ* treatment processes were discussed at the April 8-10, 2008 workshop at Hanford:

- sulfur dioxide (SO_2) and its derivatives, *meta*bisulfite, bisulfite and sulfite
- ferrous iron compounds
- electro-coagulation
- zero-valent iron (ZVI), and
- ferrous sulfide.

Each of these *ex situ* Cr(VI) reduction methods is discussed in the following sections.

4.2 SULFUR DIOXIDE/SULFITE/*META*BISULFITE/BISULFITE (S^{IV})

Sodium *meta*bisulfite ($Na_2S_2O_5$) has generally replaced sulfur dioxide and sodium bisulfite ($NaHSO_3$) as the Cr(VI) reducing agent of choice in the metal finishing industry. These $S^{(IV)}$ reducing agents have been used since before the mid-1930s. Figure 6 is a typical process schematic in which sodium *meta*bisulfite is used to reduce Cr(VI).

Reactor sizes and process control parameters shown in the figure are typical of those used when Cr(VI) is treated with reduced sulfur compounds. It should be noted that the Cr(VI) reduction rate is too low for commercial use if the pH is above ~3.0, so if this process were used at Hanford, it would be necessary to reduce the pH below 3.0, then raise it above ~10.0 to precipitate Cr(III) as the hydroxide and probably neutralize to pH ~7-8 to prevent plugging of the aquifer.

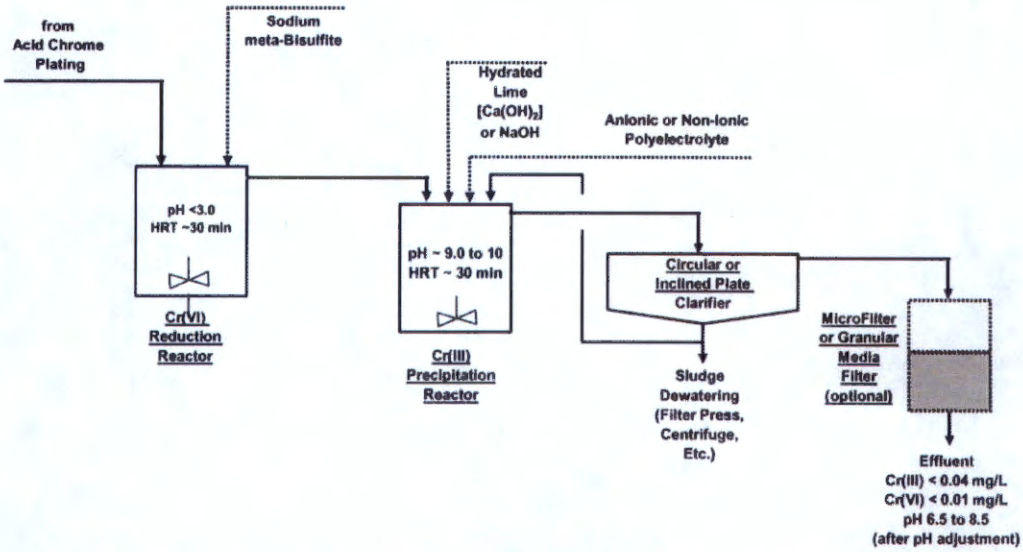


Figure 6. Schematic Diagram of Cr(VI) Reduction Process using Sodium *meta*-Bisulfite

4.2.1 Case History

A large manufacturing facility on the West Coast used sulfur dioxide in the mid-1980s to reduce Cr(VI) in ~150 to 450 gpm of rinse water, which was then discharged into a wetland. On several occasions, process upsets went undetected, leading to violations of their discharge permit.

No reliable Cr(VI) on-line analyzers were commercially available, so the facility connected an atomic absorption spectrometer (AA) to a slipstream of the treated effluent to provide early warning of pending violations. The sample collection line became plugged with post-precipitated solids, rendering the AA unit inoperable, so outside assistance to improve overall process control and monitoring was enlisted.

The process control strategy was largely retained, but key recommendations involved more frequent pH probe cleaning, manual effluent analysis and continuous flow recycle of the clarifier underflow stream back to the Cr(III) precipitation reactor to provide more reliable clarifier performance.

4.2.2 Findings and Recommendations

The following points related to Hanford application are made below.

- The Cr(VI) reduction reaction with S^{IV} compounds is too slow for *ex situ* applications, unless the pH is reduced below 3.0.
- There is little published historic information about the effectiveness of Cr(VI) reduction to very low residual concentrations, below ~10 µg/L. Most early work relied on analytical methods with significantly higher detection limits than are now

available with ion chromatography and colorimetric detection. Current methods permit Cr(VI) detection to 0.2 μg/L.

- Research is needed in areas such as reaction rates, effects of residual S^{IV} in the aquifer, and equilibrium conditions.

- Lime [$Ca(OH)_2$] produces an easier-to-settle precipitate that is also easier to dewater with centrifuges or filter presses, than caustic [NaOH]. However, caustic is easier to handle and is usually preferred by smaller facilities, despite its higher cost.

- Recycling of precipitated sludge from the clarifier underflow to the Cr(III) precipitation reactor is important for reducing $Cr(OH)_3$ super-saturation, improving solids settling rate in the clarifier, and reducing post-precipitation on downstream equipment, pipelines and in the environment.

- Nonionic or anionic polyelectrolytes are usually the most effective types for enhancing $Cr(OH)_3$ sedimentation and dewatering. Specific (empirical) testing with actual wastewater must be performed before a final polymer selection is made.

- Recently, on-line Cr(VI) analyzers have appeared on the market that are claimed capable of lower detection limits of ~4 ±2 μg/L. One such instrument is the Skalar OPA 2000, according to recent information. Frequent manual monitoring is still advisable.

- Treated water intended for re-injection should be filtered, preferably with a microfilter such as the 0.1 μm pore size devices manufactured by PALL. Multi (mixed) media filters are the only other filters might also be used.

- Considering the high pH at which $Cr(OH)_3$ is precipitated, final pH reduction to neutral conditions would probably be needed to avoid plugging of the aquifer with $CaCO_3$.

4.3 FERROUS CHLORIDE OR SULFATE (FE^{II})

Ferrous chloride and ferrous sulfate have been used to reduce Cr(VI) for many decades, pre-dating the 1930s. Ferrous iron reacts very rapidly with Cr(VI) and can be used over a pH range of ~<3.0 to ~8.0. Figure 7 is a typical process flow diagram for Cr(VI) reduction with ferrous chloride.

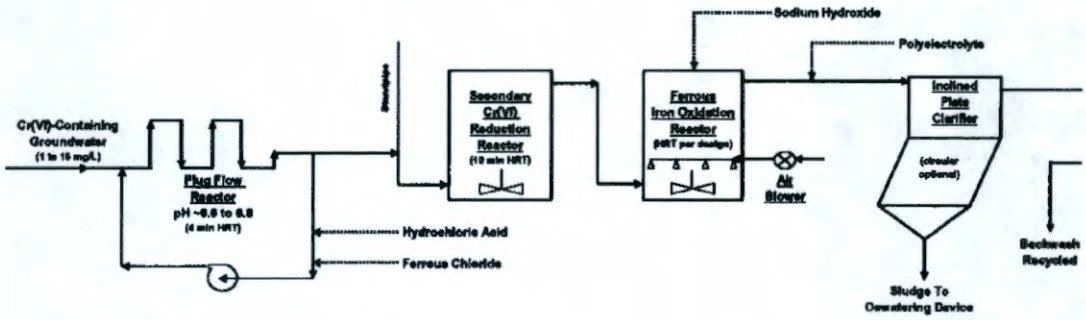


Figure 7. Schematic Diagram of Cr(VI) Reduction Process using Ferrous Iron

Ferrous chloride and sulfate, usually obtained from steel pickle liquor and as a waste product, are less expensive than if these materials were specifically manufactured from iron (or iron oxides) and the corresponding acid. Although iron-based treatment chemicals were historically relatively inexpensive, reductions in sulfur prices the past two decades have kept *meta*bisulfite and related materials cost-competitive.

Hexavalent Cr(VI) reduction with ferrous iron produces ~4 times the sludge mass as the S^{IV} reduction processes, because three moles of iron are required per mole of chromium. The cost of by-product sludge disposal is an important factor in selecting which process to use. Precipitated solids from this process typically pass TCLP criteria, but not California Soluble Threshold Limits Concentration or Total Threshold Limits Concentration criteria.

4.3.1 Case History

Groundwater beneath an industrial site in the Western United States became contaminated with Cr(VI) at concentrations as high as 15 mg/L. The site lies along a river, and when Cr(VI) appeared in monitoring wells adjacent to the river, an emergency order was issued to install a pump-and-treat system to reverse the hydraulic gradient. Discharge quality criteria were not known when design began for a 150 gpm treatment plant, but the ferrous chloride process was selected, because laboratory jar tests showed this process could reduce Cr(VI) to below the 0.2 μg/L detection limit. The design and implementation schedule did not permit pilot testing to verify performance. The plant was designed based on the laboratory tests and on reaction rate equations in two technical papers (Fendorf and Guangchao, 1996; Sung and Morgan, 1980).

Extracted groundwater is brackish (~ 6,000 to 9,000 mg/L TDS) and the initial Cr(VI) concentration in the plant influent was ~7 mg/L. After 3 years of operation, the Cr(VI) concentration has fallen to ~2 mg/L. Since startup, the plant has reduced the Cr(VI) concentration to less than the 0.2 μg/L reporting limit (ion chromatography), with rare excursions to ~1.0 μg/L. The on-line factor has exceeded 95 percent.

Figure 8 shows the laboratory test results for Cr(VI) reduction with ferrous chloride at various conditions of Fe(II) dosage and total dissolved solids (TDS).

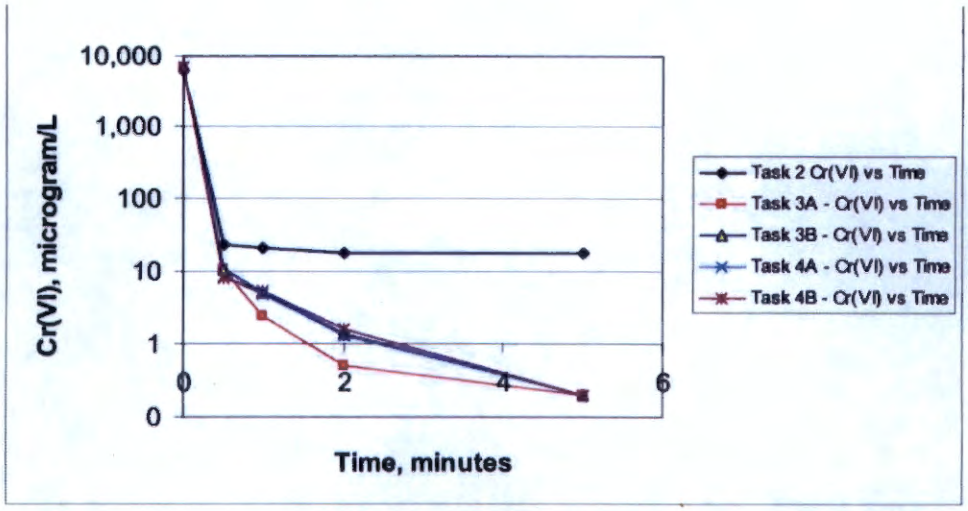


Figure 8. Cr(VI) Concentration versus Batch Reaction Time

Following Cr(VI) reduction, residual Fe(II) is oxidized with air to below ~5 to 10 μg/L, the treated water is filtered through a microfilter with 0.1 μm pores (PALL), and the water is re-injected below ground.

The two injection wells have exhibited some reduction in injectivity over the 3-year life of the facility. The wells are now under evaluation to verify how much loss of injectivity is attributable to air binding (leaky valve) and how much is attributable to fouling. Investigations are currently underway into the nature of a fine particulate fraction that was recovered during well purging and flow surging.

4.3.2 Findings and Recommendations

The following points related to application at Hanford are presented below.

- Ferrous iron [Fe(II)] chloride (or sulfate) is capable of reducing Cr(VI) in brackish water from an initial concentration of ~7 mg/L to <0.2 μg/L with high reliability.
- The treated water has always been in compliance with the 8 μg/L Cr(VI) limit and the 25 μg/L total Cr limit.
- Process control monitoring is performed manually using a HACH test kit, which has an estimated reporting limit of 10 μg/L. Recent improvements on the HACH procedure by site personnel appear to have reduced the detection limit to ~2.5 μg/L.
- On-line Cr(VI) instruments are marginally sensitive below ~10 μg/L, but recently Skalar Instruments has indicated their Model OPA 2000 can detect Cr(VI) to ~4 μg/L ±2 μg/L.
- The first-stage reactor is a plug-flow reactor, to take advantage of the fast initial reaction rate. The second reactor is a 10-minute HRT (hydraulic residence time) tank.

- The Cr(VI) reaction rate with Fe(II) exceeds that of oxygen with Fe(II) in brackish water concentrations found at the site. However, when the TDS is "low" (less than ~2,500 mg/L), it is necessary to reduce the pH to suppress Fe(II) oxidation by atmospheric oxygen. If the pH is too high, depending on the alkalinity, soluble Fe(II) can precipitate as siderite ($FeCO_3$), which makes it unavailable to reduce Cr(VI).

- Oxidation of residual Fe(II) is affected by pH, temperature, ionic strength and oxygen transfer efficiency into the liquid phase, but is able to reliably reduce the residual dissolved iron concentration to below 10 μg/L.

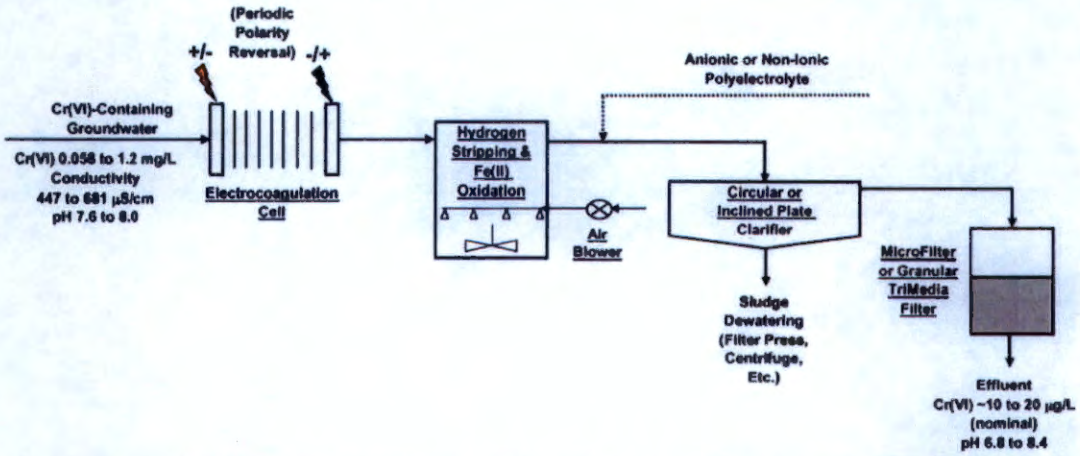
- Microfiltration through a 0.1 μm pore filter is recommended for removing suspended solids prior to re-injection. Tri-media (anthracite-silica sand-fine garnet) filtration also produces good results, but is not as effective as microfiltration.

4.4 ELECTRO-COAGULATION

The electro-coagulation process was patented in 1906. The general technique has been used for a wide variety of disparate applications such as treating rendering plant wastewater, treating grain-based food manufacturing wastewater and removing Cr(VI). A generalized process schematic is shown in Figure 9.

Figure 9. Schematic Diagram of Electro-coagulation System Process

There is little standardization for electro-coagulation design for Cr(VI) treatment applications. Actual treatment efficiency is often determined empirically, after plant startup. Electro-coagulation should be tested in each application under carefully monitored and controlled



conditions to establish efficacy. With few basic 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.

4.4.1 Case History: Hanford 100-D Area

4.4.1.1 Preliminary Technology Survey

Constraints on sulfate and chloride in treated groundwater in the 100 Area led to interest in electro-coagulation for possible use in Cr(VI) removal, because, unlike other chemical-using processes, electro-coagulation does not introduce anions into the treated water stream. Consequently, the decision was made to perform a pilot test at a flow rate of 50 gpm. During technology screening prior to the pilot test, it was found that there are very few electro-coagulation systems operating at a capacity of 100 gpm, and none were found at higher flow rates. From discussions with various electro-coagulation suppliers, there appear to be at least three mechanisms by which electro-coagulation cells reduce Cr(VI) to Cr(III):

- anodic release of ferrous iron [Fe(II)] and direct reaction with Cr(VI)
- direct Cr(VI) reduction at the cathode
- Cr(VI) reduction by hydrogen released at the cathode.

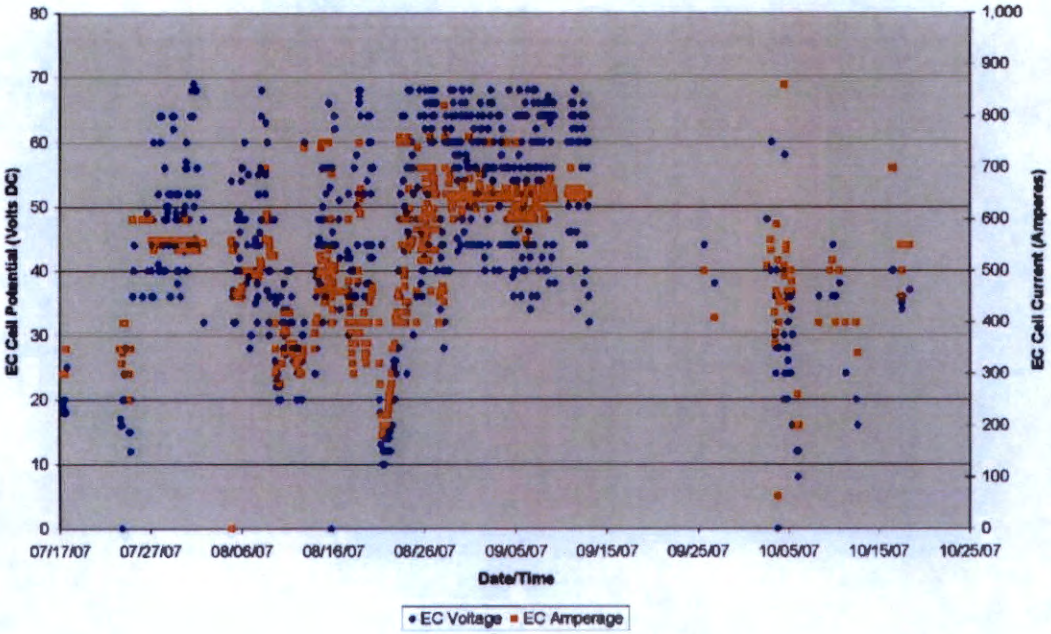
The uncertainty about Cr(VI) reduction mechanisms arises because suppliers have provided anecdotal information that either steel or aluminum electrodes are effective in reducing Cr(VI), but no controlled tests or independent corroboration were found.

4.4.1.2 Pilot Electro-coagulation Cell Operation

Pilot testing was performed for a five-month period with groundwater containing Cr(VI) at concentrations of approximately 200 to 250 μg/L. The 50 gpm pilot electro-coagulation stack is shown in Figure 10.

Figure 10. Electro-coagulation Cell with Plate-and-Frame Construction

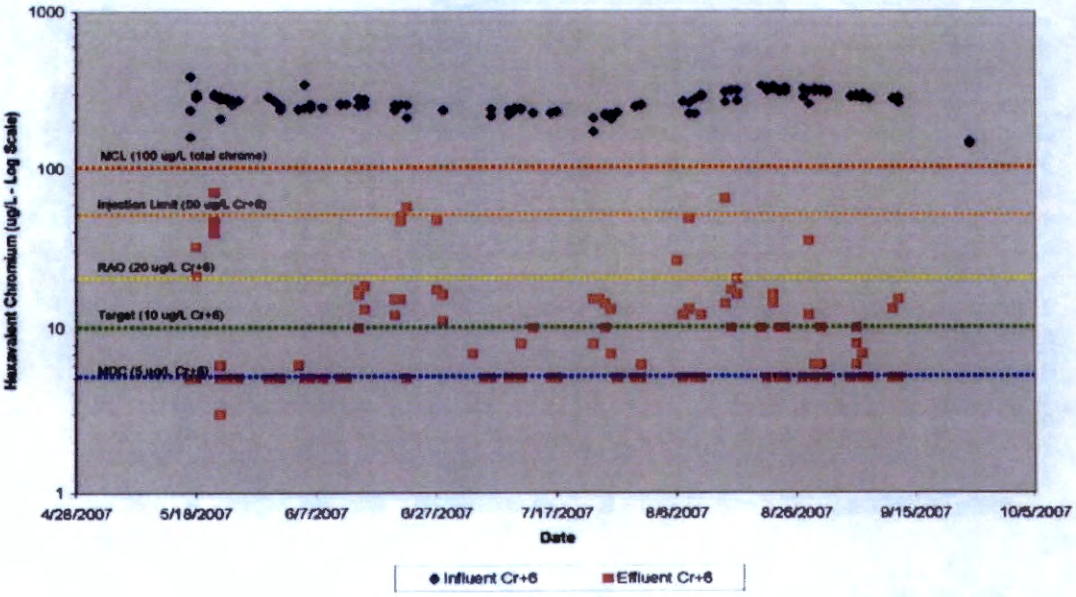
Figure 11. Electro-coagulation Cell Voltage and Amperage during Pilot Testing



For the first four days of operation, the electro-coagulation cell reduced Cr(VI) to <10 µg/L while operating 4 to 6 volts at 60 to 70 amperes and an estimated current density of 15 to 17.5 amps/ft^2 (the steel plate electrodes had overall dimensions of 2 ft x 2 ft x 0.25 in).

With ongoing operation, however, the Cr(VI) residual increased, which prompted increases in cell current, finally peaking at above 600 amperes (Figure 11). The initial current efficiency was ~1.8 percent at 60 amperes, but later efficiency dropped to 0.018 percent at 600 amperes.

Figure 12. Cr(VI) Influent and Effluent during Pilot Testing



Pilot tests showed that the Cr(VI) concentration could be reduced below the 20 μg/L treatment goal, but effluent ranged from <8 to over 50 μg/L (Figure 12). Frequent increases in cell current were needed to maintain Cr(VI) removal, because of ongoing electrode passivation. This is discussed further below.

Hydrogen may be released in sufficient quantity at the cathode that special attention should be given to potentially flammable or explosive conditions. Suppliers had different approaches for removing hydrogen. One supplier offered a "vacuum clarifier" to allow coarse and fine solids to settle and to remove hydrogen from solution. Others use aerated tanks to strip hydrogen.

During operation, anodic surfaces become scaled with iron oxide (mainly magnetite), which passivates the electrodes, necessitating increased current to sustain Cr(VI) reduction. At the cathode, alkaline scale (calcium carbonate) forms. Anode passivation and cathode scaling were addressed at Hanford by periodically reversing cell polarity, causing the cathode to become acidic, which dissolves alkaline scale, and the anode to evolve large amounts of hydrogen, which in principle dislodges iron oxide scale deposits. 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. One technical paper recommended that to avoid passivation and scaling, and to improve performance, the polarity should be reversed more frequently than every 30 to 60 seconds, and that the cells should be operated at relatively low current density.

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

Magnetite, which is a semiconductor, 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 amperes for short 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 seen in Figure 13.

4.4.2 Findings and Recommendations

- In pilot tests, electro-coagulation was able to reduce Cr(VI) to below 20 μg/L when electrodes were clean.

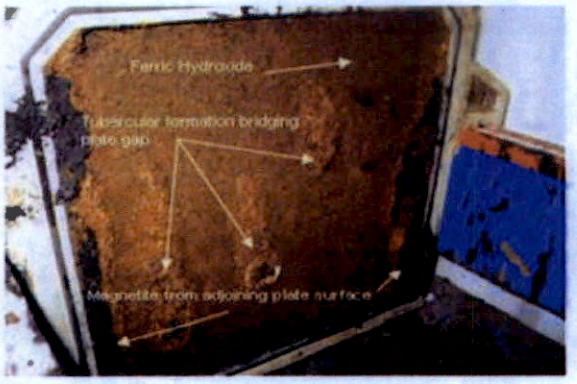
- Low current density and polarity reversal cycles as short as 30 to 60 second should be investigated as a means of reducing electrode passivation and improving performance.

- The initial current efficiency was ~1.8 percent at 60 amperes, but as electrode passivation increased, the current efficiency fell to 0.18 percent at ~600 amperes.

- Operation at high current density (~175 amps/ft^2, - initial current density was ~15 amps/ft^2) was ineffective for "burning" the passive layer off the electrodes.
- Electrode cleaning with hydrochloric acid was ineffective and did not restore cell performance.
- Cell feed 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.
- Electro-coagulation as a technology has few basic principles to draw upon for Cr(VI) removal process design purposes. Pilot testing should be performed with equipment from the manufacturer who will provide the full-scale system.
- Carefully planned fundamental investigations into the electro-coagulation process are needed to provide a firm technical basis for design and predictable performance.

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.

Figure 13. Typical Electro-coagulation Electrode Fouling

4.5 ZERO-VALENT IRON

Packed beds of steel shot (ZVI) have been used as a passive treatment for removing Cr(VI) from chrome plating rinse water. In practice, the system is very simple, as illustrated in Figure 14.

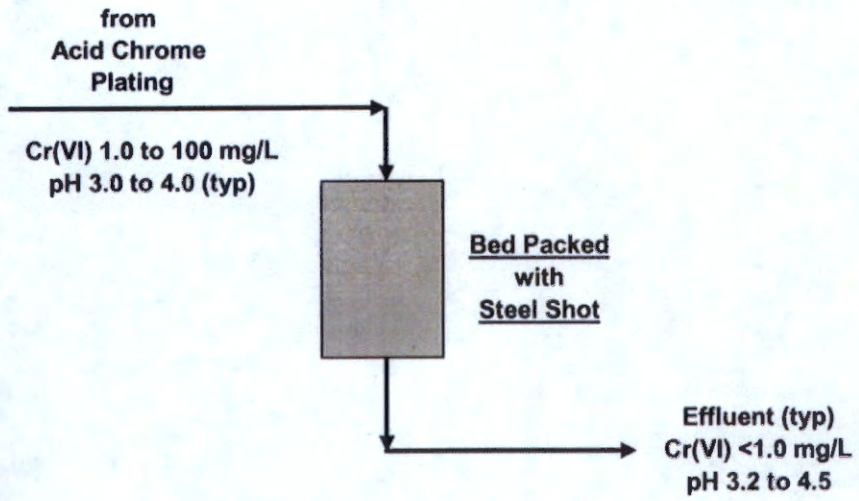


Figure 14. Passive Treatment of Chrome Plating Rinse Water in Packed Bed of Steel Shot

Chrome plating wastewater is acidic, which dissolves ferrous iron, with evolution of hydrogen. The ferrous iron reduces Cr(VI) to the tri-valent form and the effluent is neutralized with lime [$Ca(OH)_2$] or caustic [NaOH] along with other waste streams to precipitate metal hydroxides.

Packed beds of steel shot are used rarely, if at all, in contemporary facilities because the Cr(VI) concentration in the effluent cannot be controlled with sufficient precision and reliability. The steel shot tends to become coated with ferric hydroxide when the pH exceeds the ferric hydroxide solubility. To overcome ferric hydroxide coating, it would be necessary to reduce the pH below the ferric hydroxide solubility point; however, as the acidity increases, the steel shot dissolution rate increases, reducing the useful life of the steel shot.

4.5.1 Findings and Recommendations

The following points summarize the applicability of ZVI for *ex situ* treatment at Hanford.

- It would be necessary to acidify Cr(VI)-containing groundwater prior to applying it to a bed packed with steel shot to achieve reliable Cr(VI) removal.
- ZVI is not well-suited *ex situ* for treatment Cr(VI) in groundwater at Hanford.

4.6 FERROUS SULFIDE

Ferrous sulfide was investigated for use in treating metal-containing plating wastewater by the US Air Force during the late 1970s (Higgins and TerMaath, 1981). In these early studies, ferrous sulfide was manufactured on site by reacting ferrous sulfate (or chloride) with sodium sulfide (or hydrosulfide, NaHS) to produce a slurry of ferrous sulfide (FeS).

The FeS was added to plating wastewater to precipitate certain metals as insoluble sulfides and to reduce Cr(VI) for subsequent precipitation in downstream equipment.

FeS is used infrequently, if at all in metal finishing facilities, and the process was not adopted by the Air Force. The primary reasons ferrous sulfide is not used are:

- Handling of sodium sulfide and hydrosulfide, and addition of these materials to acidic solutions of ferrous sulfate or chloride raised safety concerns that were not easily addressed; and
- The process was more complex than other methods.

4.6.1 Findings and Recommendations

The following describes applicability of FeS for *ex situ* treatment at Hanford.

- FeS is not currently used for Cr(VI) treatment for safety reasons. Supplies of dry FeS have recently become available, mainly from China, but cost and availability in the US market are not known.
- FeS does appear not well-suited for *ex situ* treatment of Cr(VI) in groundwater at Hanford.

4.7 COMPARISON OF REDUCTIVE *EX SITU* TECHNOLOGIES

The five methods for reducing Cr(VI) are compared in Table 3 below, according to commercial demonstration, effectiveness in reducing Cr(VI), and scalability to flow rates that might be encountered at Hanford.

Table 3. Comparison of Technologies for *Ex Situ* Reduction Cr(VI)

Technology	Commercially Proven	Cr(VI) Reduction <20 µg/L	Scalability
Sodium *meta*Bisulfite	Yes	Yes	Yes
Ferrous Iron	Yes	Yes	Yes
Electro-coagulation	Marginal	Yes	Uncertain
Zero-Valent Iron	Yes	No	Yes
Ferrous Sulfide	Unknown	Unknown	Yes

4.8 REFERENCES

Higgins, T.E., and TerMaath, S., 1981. Treatment of plating wastewaters by ferrous reduction, sulfide precipitation, coagulation and up-flow filtration, Proceedings of the 36th Industrial Waste Conference, May 12, 13 and 14, 1981, Purdue University, Lafayette, Indiana.

Fendorf, S., and Li, G., 1996. Cr (VI) reduction by Fe(II). Environmental Science and Technology 30:1614-1617.

Sung, W., and Morgan, J.J., 1980. Fe(II) oxidation by atmospheric oxygen. Environmental Science and Technology 14:5:561-568.

5.0 EX-SITU TREATMENT ALTERNATIVES BASED ON DISCHARGE OPTIONS

By Ronald Borrego, P.E., Geomatrix Consultants, Inc.

5.1 STATEMENT OF PROBLEM

Due to past operations at many industrial sites around the world, chemical releases have reached groundwater, creating contaminant plumes that must be addressed to mitigate impacts to groundwater that may be used for agriculture, industrial uses, or municipal drinking water. For groundwater contaminated with chromium, several issues maydefine the action necessary to mitigate the impacts and address the concerns raised by regulatory agencies. The issues could include the following.

- Chromium is found in the groundwater at levels in excess of regulatory limits.
- Chromium is impacting use of the groundwater supply or impacts are imminent.
- Replacement water supply or treatment of extracted water to remove chromium is needed to contain the plume and perform mass removal of chromium.
- What options are available for discharging extracted water after chromium is removed?

5.2 POSSIBLE DISCHARGE ALTERNATIVES

Impacted groundwater can be extracted and treated using new or existing wells. Once treatment is complete, the following are examples of options for discharge of treated groundwater:

- Discharge to a waterway
- Municipal drinking water
- Urban green space irrigation
- Agricultural reuse
- Industrial reuse
- Wetlands creation or maintenance
- Aquifer recharge

A short discussion on each of these discharge alternatives is presented later in this section.

5.3 TREATMENT GOALS

The Environmental Protection Agency (EPA) has established the MCL for total chromium at 100 parts per billion (ppb). State-level health departments and the World Health Organization (WHO) have reduced the MCL even further to 50 ppb. The effect of Cr(VI) ingestion is

subject to differing scientific opinions, and there are currently no individual Federal or State drinking water standards for Cr(VI). Only total chromium has been regulated in drinking water, and investigations are underway to gain knowledge related to Cr(VI) treatment options.

In recent project work, the following total chromium treatment goals were negotiated with a variety of Federal and State agencies for different discharge options (Table 4).

Table 4. Total Chromium Treatment Goals

Discharge Alternative	Total Chromium Treatment Goal
Discharge to a waterway	100 ppb[1]
Municipal drinking water	50 ppb[2]
Urban green space irrigation	50 to100 ppb
Agricultural reuse	100 ppb
Industrial reuse	50 ppb
Wetlands creation or maintenance	??[3]
Aquifer recharge	50 ppb

[1] Hardness dependent Cr(III) and Cr(VI) standards may apply; Cr(VI) may be < 10 ppb

[2] Cr(VI) not currently regulated, but may be 5 ppb when regulations implemented

[3] Cr(III) treatment level hardness dependent, Cr(VI) < 10 ppb

5.4 AVAILABLE *EX SITU* TREATMENT TECHNOLOGIES

Each of the *ex situ* treatment technologies presented have been selected, because of promising bench-scale or pilot-scale testing, or have demonstrated performance in full-scale treatment. Many of the tests have been performed as chromium specific treatment and have not considered the effects of co-contaminants. However, chromium is often found in groundwater where other contaminants are present. These co-contaminants that can block or reduce treatment effectiveness include nitrate, sulfate, phosphate, total dissolved solids, silica, arsenic, selenium, uranium, vanadium, and fluoride. The evaluation of any treatment technology must consider the effects of these co-contaminants.

Federal and State agencies have approved the following *ex situ* treatment technologies for removing total chromium from drinking water supplies:

- coagulation/filtration
- ion exchange
- reverse osmosis
- lime softening.

The following *ex situ* treatment technologies have been identified as potential alternatives:

- electrochemical precipitation using ferrous iron

- electrodialysis reversal – electro-coagulation
- adsorption/chelation
- biological treatment.

Other treatment technologies await further research and confirmation testing, and thus, are not ready for full-scale implementation for chromium treatment at this time.

Pilot testing to evaluate the effectiveness and viability of technologies available for the removal of Cr(VI) to low levels in drinking water is currently being performed at the Castaic Lake Water District in Santa Clarita, California and the City of Glendale California. These studies are evaluating the effectiveness and cost of providing Cr(VI) removal to 20, 10, 2, and 0.2 ppb.

5.4.1 Brief Description of Available Treatment Technologies

The following information provides a brief description of available technologies for treatment of Cr(VI).

5.4.1.1 Coagulation/Filtration

This treatment process reduces Cr(VI) to Cr(III) with Fe (II) followed by hydroxide precipitation and filtration. This technology has demonstrated effective Cr(VI) removal to < 20 ppb, while generating a sludge that requires off-site disposal.

5.4.1.2 Ion Exchange

This treatment process typically has used regenerable strong base resins (SBR), as they have performed better in testing than one-pass disposable weak base resins (WBR). The SBR resin is regenerated off-site with a sodium hydroxide brine elution process, and the solution used to regenerate the resin requires treatment. A periodic acid or caustic wash of the resin is required to completely strip chromium from the resin, followed by normal brine regeneration. New testing with regenerable WBRs have shown that if the pH can be maintained near 6 SU, effective Cr(VI) removal is possible. This technology has demonstrated effective Cr(VI) removal to 2 ppb. The SBA resin generates a waste from the treatment of the regenerate solution, and the WBA resins are disposed off-site, potentially as a hazardous waste.

5.4.1.3 Reverse Osmosis

This technology effectively removes Cr(III) and Cr(VI) to 2 ppb. Pretreatment may be necessary to prevent fouling or scaling, and is intended to control hardness, iron, manganese, silt, and turbidity. The reverse osmosis system produces a 15% to 20% reject waste stream that requires disposal.

5.4.1.4 Lime Softening

This technology uses calcium, magnesium or sodium carbonate to reduce water hardness, and precipitates a calcium, magnesium or sodium hydroxide precipitate along with chromium precipitates. The pH is adjusted to approximately 10.5, resulting in hydroxide precipitation, which is followed by filtration. This technology generates a sludge that requires off-site disposal. Lime softening is effective for removal of Cr(III), but performs poorly when

removing Cr(VI). Cr(VI) can be reduced to Cr(III), but concerns with re-oxidation of back to Cr(VI) make this technology potentially unreliable for treatment of Cr(VI) to levels below 10 ppb.

5.4.1.5 Electrochemical Precipitation using Ferrous Iron

This technology uses Fe (II) to reduce Cr(VI) to Cr(III), with pH adjustment followed by precipitation, flocculation, and filtration to effectively remove total chromium to 50 ppb. No data were available for treatment performance on an effluent containing only Cr(VI). Filter residuals require off-site disposal.

5.4.1.6 Electrodialysis Reversal – Electro-coagulation

These technologies have performed well in similar treatment applications and for that reason are presented here as a potential technology for future consideration. Only limited data are available for evaluation of performance in chromium treatment. Section 4 describes the results of an electro-coagulation demonstration for treatment of chromium at Hanford.

5.4.1.7 Adsorption/Chelation

Pilot testing of this technology has used both sulfur modified iron and proprietary Magnetic Ion Exchange (MIEX®) as adsorption media. This process uses iron to either adsorb or reduce Cr(VI) to Cr(III) followed by filtration to reduce chromium to levels < 20 ppb.

5.4.1.8 Biological Treatment

This technology uses either continuous flow or batch reactors to use biological mechanisms to reduce Cr(VI) with a biofilm using various filter media types. This technology generates a biological sludge that requires off-site disposal, and is capable of reducing chromium concentrations to < 20 ppb.

5.4.2 Treatment Considerations

The following points must be considered when evaluating groundwater treatment alternatives.

5.4.2.1 Groundwater Ownership

Groundwater can either be privately owned or publicly owned, depending on the State. Correlative groundwater rights are an ownership right similar to riparian rights in a surface water supply. This right is appropriated based on the size of surface area of land a land owner possesses. These water rights may be sold to individuals or groups with high water demands without large land holdings. Examples would be cities or agricultural irrigators. In many western states, groundwater is allocated through an appropriative system and is based on a calculated sustainable yield, subject to increase or decrease on any given year.

In Washington State, the water collectively belongs to the public and cannot be owned. A beneficial water right authorizes a pre-defined quantity of public water for a designated purpose. Water users exempt from this permitting system include stock watering, domestic uses, industrial purposes, and lawns/gardens under ½ acre. Washington State has also implemented the Critical Aquifer Recharge Ordinance (CARA) to provide adequate recharge and protection to aquifers used as a potable water supply. To determine the effect of aquifer

impacts and extraction/treatment needed, research to determine all water users affected must be completed so the options for water discharge can be correctly evaluated.

5.4.2.2 What is the Primary Driver for Action?

The drivers for an organization can range from voluntary action to response to a regulatory order issued by a State or Federal regulatory agency. The driver initiating action for a remediation effort will likely define the treatment level needed, timeframe for treatment, documentation required and the permits necessary.

5.4.2.3 Will Waste Streams be Generated?

All treatment technologies will generate some kind of waste stream. The volume of the waste stream and the disposal options related to its hazard level can dramatically affect the treatment cost. Consideration of anticipated waste streams, disposal options and costs is critical in the early stages of technology evaluation.

5.4.2.4 How Quickly Must Treatment /Containment be Implemented?

Some of the treatment technologies presented in this report are simple and can be implemented quickly with limited pilot testing. Other technologies have long-lead equipment times, and may require significant testing to gather needed scale-up data before design and procurement of the system can begin.

5.4.2.5 How Long Must Treatment Remain in Operation?

Will this treatment system be required to operate for a short time or must it be in place for a 20 or 30 year service life? If the system is to be in place for a long time, a more substantial system design, as well as additional capital costs and the need for equipment redundancy to limit the amount of treatment downtime are likely to be required.

5.4.2.6 What are the Permitting Requirements?

The needed permits and approvals to construct from the participating regulatory agencies could involve a significant processing time. Discharge options such as waterway discharge and municipal drinking water use may also involve a lengthy public review and comment period. Permitting limitations could weigh heavily in the selection of a treatment technology.

5.4.2.7 Are There any Funding Limitations?

Limited availability of capital funds to construct a treatment system or a limited amount annual funding to support operations and maintenance costs may also affect the decision when choosing a treatment technology.

5.5 DISCUSSION OF DISCHARGE ALTERNATIVES

The technology chosen to remove chromium from impacted groundwater will not be evaluated on the merits of the technology alone, but will consider co-contaminants present and the need to provide treatment for them, and on the available options for treated water discharge. The following are brief discussions of options for discharge of treated groundwater:

5.5.1 Discharge to a waterway

This alternative will require a National Pollutant Discharge Elimination System (NPDES) permit, and may involve a State Environmental Policy Act (SEPA) process with a public review and comment process. There will be strict water quality goals that will limit choices for treatment technologies. If the waterway is located close to the treatment site, limited infrastructure will be required to convey the treated water to an outfall structure.

5.5.2 Municipal drinking water

This process will extract impacted groundwater and treat it to drinking water standards for delivery to municipal water users. Many private corporations will not want the exposure to the potential legal risks with this alternative. Because this option involves the use of a severely impacted resource for municipal use, there will be a lengthy permitting process and public review and comment period before the system can deliver treated water to the public.

5.5.3 Urban Green Space Irrigation

This alternative provides a good route for discharge during periods of seasonal demand to serve golf courses, cemeteries, school grounds, parks, parkways, etc. During periods of rain or during winter months, an alternate method such as discharge to surface water is likely to be needed. There may be strict water quality requirements to match reuse water in an existing distribution system. Also, there may be a public review and comment process for this alternative. Because reuse irrigation water may already be used throughout a city, the existing distribution system may be used and the connection to the existing system would then be the only infrastructure construction required.

5.5.4 Agricultural Reuse

Like urban green space irrigation, this alternative provides a good route for discharge during periods of seasonal demand. During periods of rain or during winter months, an alternate method such as discharge to surface water is likely to be needed. There may be strict water quality requirements depending on the crops being irrigated. The Food and Agriculture Organization of the United Nations (FAO) issues water quality guidelines for irrigation. Because the water must be delivered to several agricultural plots, there may be significant infrastructure costs. Also, agricultural land adjacent to urban areas is subject to development, so this may not be a viable long-term alternative.

5.5.5 Industrial Reuse

This alternative delivers treated water to industrial customers for use in cooling or process applications. There may be existing infrastructure in place, so implementation costs may be reasonable. The industrial demand may be variable over time, and may not be a reliable long-term alternative. Also, a local municipality may have difficulty using all reuse water they produce on low demand months, and there may be competition with a city utility to discharge water. The water quality requirements for this alternative may be similar to drinking water treatment levels.

5.5.6 Wetlands Creation or Maintenance

This alternative will require a NPDES permit, and may involve a State Environmental Policy Act (SEPA) process with a public review and comment process. There will be strict treatment goals that will limit choices for treatment technologies. This discharge can be used to create constructed mitigation wetlands or restore degraded natural wetlands. It is likely that this alternative could be permitted for year-round discharge.

5.5.7 Aquifer Recharge

This alternative can be implemented using infiltration basins, infiltration galleries or injection wells. It will likely require an Underground Injection Control Program (UIC) Permit and a Waste Discharge Permit containing anti-degradation water quality limits and Washington State will limit the discharge with the Critical Aquifer Recharge Area Ordinance (CARA). The quality of treated water, the chemistry of the receiving groundwater and mineralogy of the aquifer will all contribute to the success or failure of an aquifer recharge project. Careful analysis of injected water effects is needed to ensure success. There are currently three demonstration projects and four projects in planning and design using this approach in Washington State

5.6 SUMMARY

The need to provide efficient and cost-effective treatment to remove total chromium and Cr(VI) from impacted groundwater supplies is an increasing problem for private industry as well as Federal and State agencies. Numerous treatment technologies exist for the removal of chromium from groundwater. These treatment costs could range from $1.50 to $18.00 for every 1,000 gallons treated. The trend in permitted concentration levels of Cr(VI) in discharged water is decreasing over time, and is 5 ppb for discharge options like discharge to a waterway and wetlands. Several other discharge options may be available, depending on the location of the treatment system and the level of treatment provided. Many involve lengthy permitting and public comment periods, and many may not represent reliable long-term discharge solutions. Aquifer recharge is a popular alternative, and this alternative will require treatment to near drinking water standards. The success of an aquifer recharge program will rely on a thorough understanding of the treated water quality, chemistry of receiving groundwater and the mineralogy of the aquifer materials.

The selection of a treatment technology to reduce chromium levels in a groundwater supply will require a complete evaluation of co-contaminants and the effect they will have on treatment, will include bench and pilot testing to ensure a complete understanding of the treatment limitations with extracted water chemistry, and finally must be evaluated in the context of the selected discharge alternative.

This page intentionally left blank

6.0 CHROMIUM TREATMENT IN GROUNDWATER AT THE DOE PANTEX PLANT, AMARILLO TX

By Chris Lyles, DOE Pantex

6.1 BACKGROUND

The Pantex Plant is a DOE/National Nuclear Security Administration facility located in Amarillo, TX. Pantex has a long-term mission to maintain the safety, security, and reliability of the nation's nuclear weapons stockpile. B&W Pantex, the management and operating contractor at Pantex, maintains, builds, and retires nuclear weapons in support of our nation's nuclear deterrent. The Environmental Projects and Operations (EP&O) Division is responsible for the investigation and cleanup of the corrective action units at Pantex Plant.

Figure 15. The Pantex Plant near Amarillo Texas

Pantex sits on approximately 16,000 acres of land, with 4,000 acres of that being dedicated to actual production facilities and processes. The "buffer zone" around the plant consists of mainly agricultural farmland that is managed by Texas Tech University.

6.2 GROUNDWATER

Two distinct aquifers are present under the Pantex Plant. The shallow aquifer, called "the perched groundwater," is created by water pooling on a thin fine-grained zone (FGZ) at an average depth of about 276 feet bgs. This aquifer is rather thin (average thickness is about 7 feet) and the horizontal extent is limited. The deeper aquifer, called the Ogallala Aquifer, is extensive laterally and significantly thicker than the perched groundwater. The Ogallala is limited in depth by what is referred to as the red bed formation. This formation slopes downward from south to north, at depths ranging from about 350 to 820 feet bgs. Vertical flow between perched groundwater and the Ogallala Aquifer is limited by the presence of the FGZ. Downward movement of perched groundwater through the FGZ to the Ogallala Aquifer varies area to area, but generally increases toward the south and east near the edge of the perched groundwater.

6.2.1 Groundwater Impacted with Chromium

Two primary contaminants exist—chromium and high explosives. However, this section describes only the chromium plumes and current remedial solutions.

Two chromium plumes with source areas beginning in Zone 12 South have been identified. A cooling tower used in the production of high explosives is the source for one plume, while the other originates from an area that previously housed chrome plating operations. Both plumes

are moving in a southeasterly direction within the perched groundwater. The presence of chromium has not been detected in any of the Ogallala Aquifer monitoring wells installed to monitor these two plumes. Within the perched groundwater, concentrations of chromium up to 5,000 ppb have been measured.

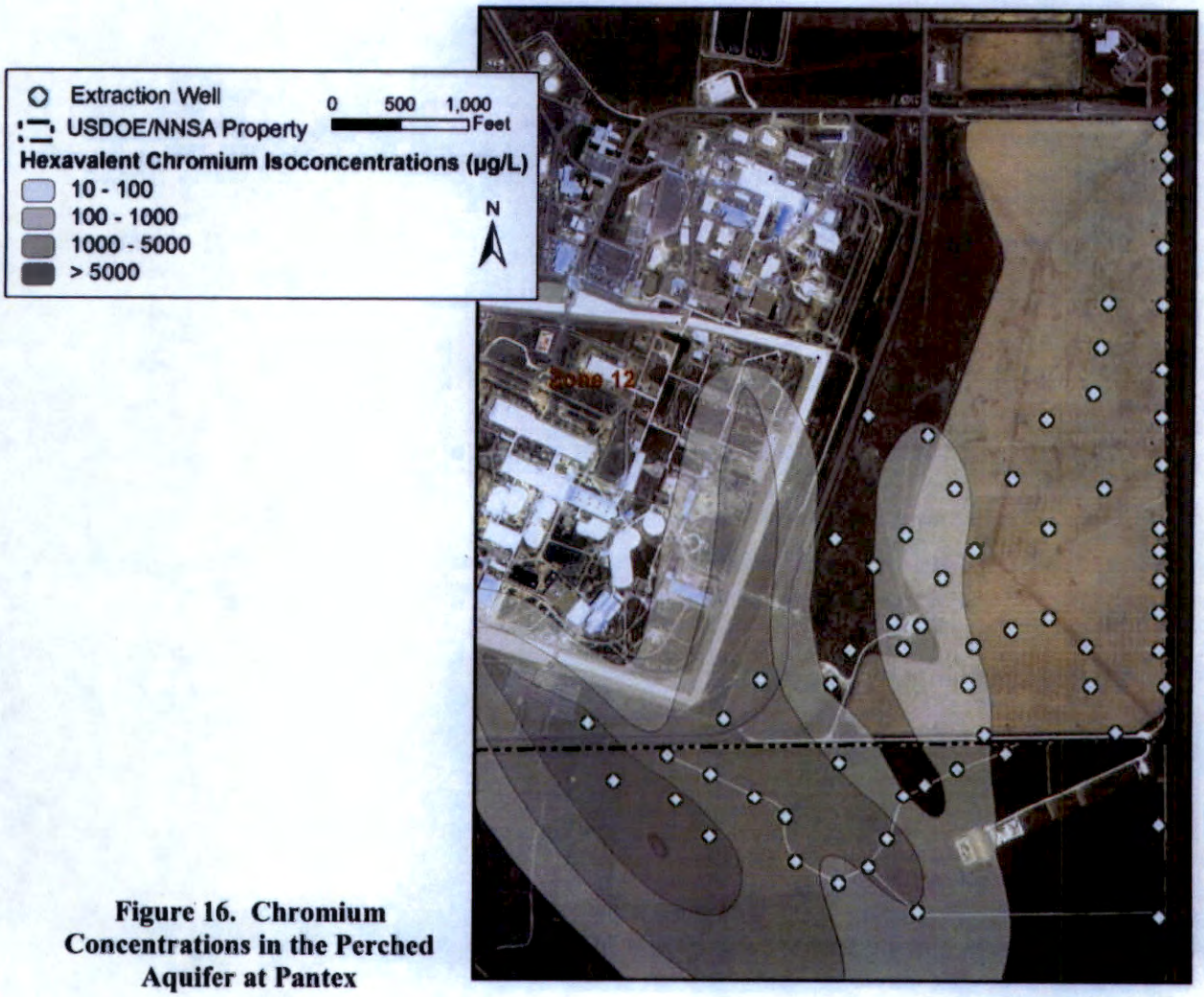


Figure 16. Chromium Concentrations in the Perched Aquifer at Pantex

6.2.2 Corrective Measures Implemented for Chromium Treatment

A P&T system has been installed in Zone 12 at the Plant for the extraction of high explosives, with chromium as a secondary contaminant. Approximately 400 gpm of groundwater is extracted from wells, filtered by granulated activated carbon, and treated using ion exchange. The treated effluent is currently reinjected, sent for beneficial use on Texas Tech agricultural land, or sent to the *in situ* bioremediation project for process water. The preferred option is use on agricultural land, but an ion exchange treatment system to remove boron must be used on

this water to produce a desirable quality for crop use. As part of a final corrective remedy, a conveyance pipeline is being installed for transport of the water to a local power company that will use the treated water in their cooling towers. The 11.5 mile conveyance line is scheduled to be installed by September 2008, allowing all of the treated water, as well as all industrial process water from the Pantex Plant, to be transported to a coal-fired power plant.

Playa 1, where a playa lake responsible for recharge to the perched aquifer is located, currently has a hydraulic "mound" of water beneath it that recharges the perched aquifer and promotes flow to the southeast and off the Pantex property. This flow of the perched groundwater is towards an area where the FGZ is very thin, or non-existent, thus potentially impacting the Ogallala Aquifer. A second P&T facility that will use 15 extraction wells is being installed at Playa 1 to minimize recharge to the perched aquifer and further offsite impacts.

Groundwater fate and transport modeling predicts that within the next 20 years there is a possibility that perched groundwater may impact the Ogallala Aquifer if nothing is done in the southeast area of the site. This area is known to have a very thin, or non-existent FGZ.

Three *in situ* technologies were pilot-tested as a redundant treatment system to be installed to address any perched groundwater that could flow into the area where the FGZ is thin or not present. The three technologies tested included: emulsified soybean oil (Newman's Zone), sodium dithionite, and CaS_x. Results of these tests demonstrated that the emulsified soybean oil was the best alternative, providing a low-cost, implementable solution. Both the sodium dithionite and the CaS_x would have required much closer well spacing for effective delivery and were much higher cost materials, which together would have resulted in a much higher cost alternative.

To create a bio-reducing zone in the southeast area, 46 injection wells were installed. The injection grid is based upon a one hundred foot well spacing with three rows of wells, Figure 17.

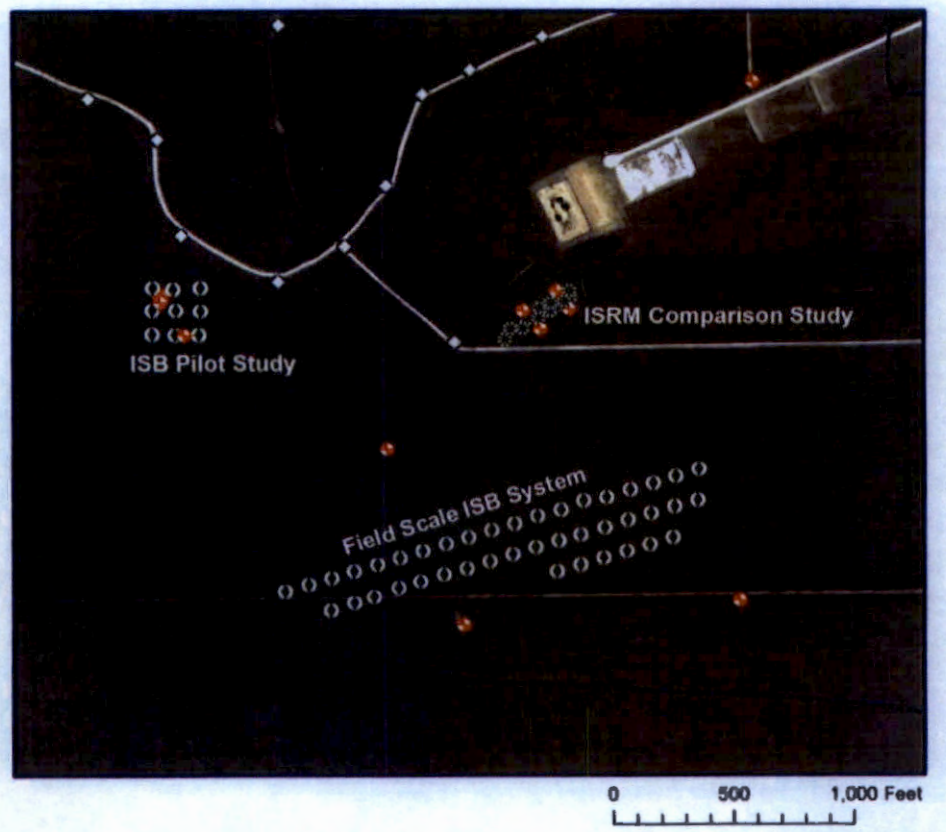


Figure 17. Injection Well Grid for the *In Situ* Treatment Area in the Southeast Portion of the Pantex Site

Figure 18. Chromium Concentrations over Time during Emulsified Soybean Oil Pilot Study

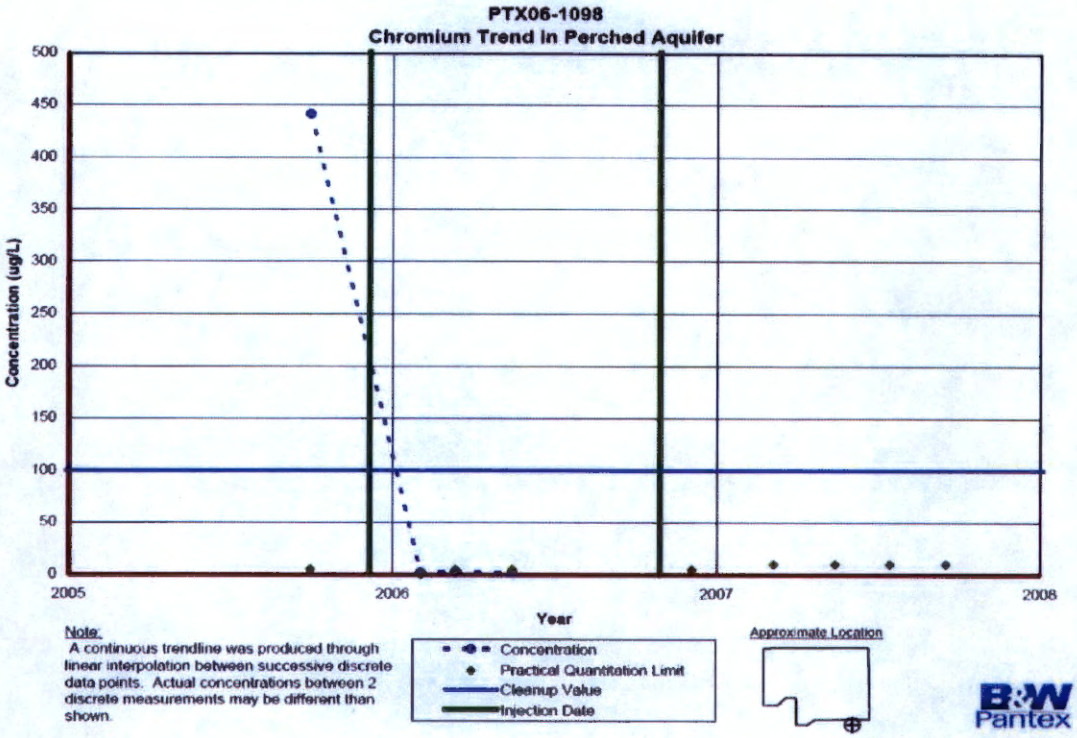
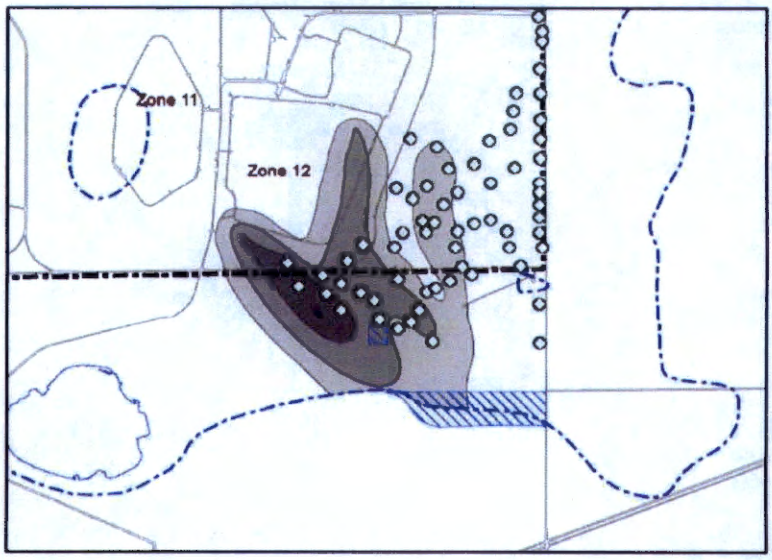


Figure 19. *In Situ* Treatment Area Overlain on a Map of Chromium Concentrations (blue hatched lines)



6.2.3 Lessons Learned

Lessons learned from this project include the following.

- A CORE team approach was used for all regulatory decisions and worked very well, as the members worked very closely throughout the entire project. Pantex is both a CERCLA and RCRA regulated site; therefore, both State and Federal regulators has authority over the site. The CORE team consisted of the project manager for the Texas Commission on Environmental Quality, project manager for the EPA, Pantex Site Office Project Manager, and division manager from B&W Pantex. Teleconferences were held weekly to promote communication and team-building; face-to-face meetings were also conducted on a regular basis.

- Pilot-scale studies must be conducted prior to implementation of any field-scale corrective remedy. Money, time, effort, and stakeholder confidence all benefit from pilot-scale studies—not to mention the taxpayers.

- New ideas should be encouraged early in the process. The current plan to transport the treated water to the local energy producer was developed very late in the process, thus costing time and additional money to implement on a fast-track schedule. This is the best alternative, but having the idea a year earlier would have been preferable. Now, environmental assessments are being rushed and the construction phase started later than expected.

- Be very open with the regulators and public from the beginning, if possible. If you build their trust and confidence early in the process, their involvement will hopefully help you close the site expeditiously.

7.0 OVERVIEW OF PNEUMATIC INJECTION OF ZERO VALENT IRON FOR IN-SITU CR(VI) REDUCTION

By Tom Simpkin, Ph.D., P.E., CH2M HILL

7.1 TECHNOLOGY OVERVIEW

This technology involves the injection of powdered Zero Valent Iron (ZVI) in a water-based slurry into the subsurface target treatment zone (TTZ). The basic process has two steps 1) initial nitrogen gas injection that may induce pneumatic fracturing and 2) atomized slurry ZVI injection with nitrogen gas as a carrier fluid. In low-permeability geologic materials, pneumatic fracturing of the TTZ media is often conducted by injecting the gas at sufficiently high pressures to create a fracture network, prior to injection of the reactive powder. This two-step process allows for the atomized slurry to be injected using much lower pressures than conventional hydraulic injection and results in better distribution of the material within the subsurface. The technology has been developed and is patented and by ARS Technologies (http://www.arstechnologies.com/index.html).

High volumes of gas, more than 1,000 scfm, are injected during both the initial fracturing phase and during the atomized injection phase. The pressure used will depend on the depth and the type of geological material. If fracturing is desired, pressures of more than 150 psi are typically used. After the initial fracturing, injection pressures may fall, but may remain greater than 100 psi.

Based upon the physical characteristics of the geology where the injections are applied, the actual emplacement mechanism of the ZVI powder will vary. These mechanisms can be characterized into three categories; dispersion, fluidization, or fracture filling.

- In porous (coarse) materials such as gravel, the injection of iron powder will result in the dispersion around soil or rock particles, and will travel as far as the fluidization energy of the gas carrying the particle maintains enough velocity to keep it from settling. Under this scenario, the injection of high volumes of gas and atomized slurry will result in local fluidization or movement and mixing of the ZVI particles within geologic material.

- In finer more cohesive soils such as silts and clays, the high volume/pressure injections result in the inducement of fracturing within the formation. Under this mechanism, the emplacement of iron will be governed by the flow of gas within the fractures and the iron particles will settle into the created fracture network as their velocity decreases.

Under field conditions where natural geologic heterogeneities are inherent to any formation, the actual emplacement will typically consist of all three types of emplacement mechanisms. The emplacement is likely to create a fingering or branching pattern of distribution of ZVI and injection locations are sited to achieve as interconnected a distribution pattern as practicable

Pneumatic injections are done in newly drilled boreholes because the pneumatic injection cannot be performed through a well screen. A casing may be used to keep the boring open, and

only the portion being fractured (typically isolated by inflatable packers in 2-ft increments) is exposed to the specialized fracturing nozzle. Figure 20 illustrates the equipment and Figure 21 is a photo showing the atomization of slurry at the injection nozzle.

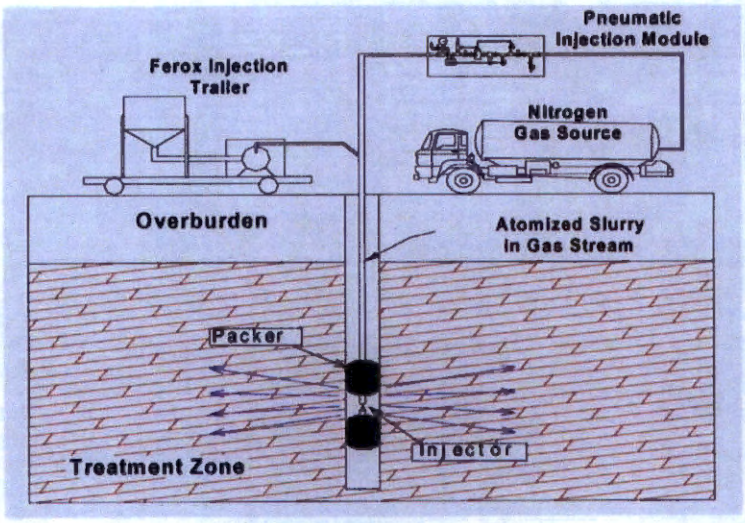


Figure 20. Pneumatic Injection Process

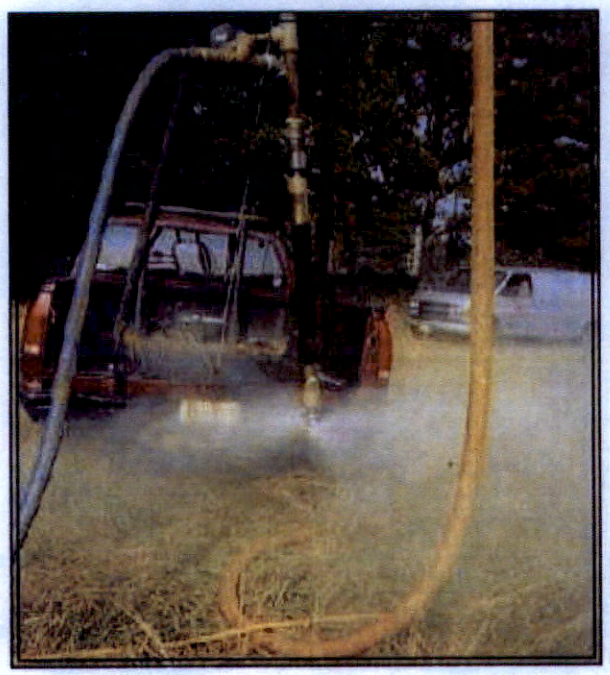


Figure 21. Slurry Atomization

The ZVI typically used for this approach may be considered powdered, or micron-scale, with particle sizes in the range of 60 to 100 um. These particles are large enough that they will not move through typical soil pores without fracturing or the assistance of the high energy of atomization. This micron-scale ZVI is smaller than the size range typically used for

conventional ZVI Permeable Reactive Barriers (PRBs), which is usually in the range of 200 to 2,000 um. Nano-scale ZVI is in the range of 0.001 to 0.3 um, which makes it small enough that it has the potential to move through soil pores during injection without any type of fracturing. However, there are many other challenges with nano-scale ZVI, which is typically more expensive than micron-scale ZVI.

Pneumatic injection of ZVI can be used to treat a source zone (high concentrations of contaminant where the release originally occurred), a dissolved plume, or as a barrier to reduce further migration. A barrier application would involve a line (or overlapping lines) of injection wells to create a flow-through treatment zone.

7.2 TECHNICAL BASIS

The chemistry of the Cr(VI) reduction with ZVI may involve a number of process including:

- direct reduction of Cr(VI) to Cr(III) at the surface of the ZVI, forming chromium oxides that may coat and reduce the reactivity and longevity of the ZVI (called passivation)

- reduction of Cr(VI) by Fe(II) that is produced from the oxidation of the ZVI by water (Because the Fe(II) is soluble, the Cr(VI) reduction may take place away from the surface of the ZVI particle)

- biological reduction of Cr(VI) using hydrogen or Fe(II) as the electron donor (Hydrogen and Fe(II) are produced from oxidation of ZVI; this biological Cr(VI) reduction mechanism may also take place away from the ZVI particle.)

When exposed to oxygen (either dissolved in water or in air), the ZVI will also be oxidized. The ferric hydroxides produced from this reaction will coat the ZVI particles when this happens (another form of passivation). Passivation may reduce the rate of the reactions of the ZVI with Cr(VI) and other species. Repeated exposure to oxygen will lead to consumption of the ZVI and extensive passivation. ZVI will also react with all nitrate present in the groundwater, reducing it to nitrite and then ammonia.

The mass of ZVI injected should be based on stoichiometric considerations, but there may be some minimum ZVI dose to be effective. The stoichiometry should be estimated based not only on the Cr(VI) present, but also on the presence of oxygen, nitrate and other oxidized compounds that may react with the ZVI. In a barrier approach, the flux of these oxidants should to be considered. The minimum dose may be based on providing sufficient distribution of ZVI particles such that the distance between adjacent particles is minimized, enhancing the probability of Fe(II) treatment of contaminants within the TTZ. The minimum ZVI dose is now considered to be something of about 0.5 percent or greater (weight of ZVI to weight of soil in the target zone).

7.3 STRENGTHS AND WEAKNESSES

The greatest strength of pneumatic injection of ZVI is that it offers a method of delivering a fairly high dose of ZVI into a variety of subsurface media without using extremely aggressive approaches, such as the trenching for PRBs or using soil mixing equipment. Because dedicated injection borings are used, the ZVI maybe emplaced much deeper than can be achieved with

conventional trenching equipment. Additionally, injection technology can be safely applied beneath or in close proximity to structures, resulting in less surface disruption.

The primary weakness of pneumatic injection of ZVI is the uncertainty regarding the distribution of the ZVI in the subsurface (thus, providing sufficient contact with target contaminants). It is the distribution of the ZVI which will drive the success of the technology. Although the equipment and techniques for the pneumatic delivery have improved over the past 10 years, it is still difficult or impossible to predict the distribution of the ZVI without field trials and inferences from core samples. These same statements can be made about any technology that involves the injection of treatment materials into the subsurface. However, the pneumatic injection delivery method may result in improved distribution in low permeability formations.

7.4 OPTIMIZATION OF THE TECHNOLOGY

Optimization of the technology involves varying the ZVI dose and the injection methods and approaches. Optimization of the injection methods and approaches may involve varying the gas and liquid flow rates, the drilling methods, and the equipment used during the injections. For example, the packers that seal the injection interval are critical to directing gas flow into the formation and not back up the soil boring.

7.5 LIFE CYCLE COSTS

The primary cost components of the technology include:

- Drilling
- ZVI
- Nitrogen gas
- Injection equipment lease
- Labor for injections

Historic costs for the injections have ranged from $4.15 to $17 per lb of ZVI emplaced. This will be very specific on the depth of injection and other site specific conditions.

There are no operations cost with this technology. However, the ZVI is likely to have a finite life, which will be a function of the environmental conditions. For example, a fluctuating water table is likely to shorten the life of the ZVI in the zone that is exposed to air and the frequently oxygenated groundwater.

7.6 GENERAL PERFORMANCE SUMMARY

CH2M HILL has applied this technology at 12 sites, which include pilot and full-scale applications. The target contaminants were mostly chlorinated solvents, but one site had Cr(VI) as the primary contaminants. The data available from these sites are far from ideal, but do allow some qualitative analysis of the performance. Table 5 is a summary of a qualitative analysis.

Table 5. Summary of Performance at Field Sites

Site	Depth		Fracturing occurred in sat zone		ZVI Distribution		Performance	
	<35	80-100	No	yes	poor	good	poor	good
1	1		1			1		1
2	1		1			1		1
3	1			1		1		1
4	1			1		1		1
5	1			1		1		1
6		1		1		1	1	
7		1	1			1		1
8	1		1		1		1	
9	1		1		1		1	
10	1							
11		1		1		1		1
12		1		1	1		1	
Total	**8**	**4**	**5**	**6**	**3**	**8**	**4**	**7**

Fracturing was indicated by a pressure response curve that had a peak with a rapid decline to a maintenance pressure. Fracturing was noted in just over half of the sites.

ZVI distribution was either noted through qualitative or quantitative observation of iron in soil cores, inferred from measured pressure distributions, or through changes in key groundwater indicators such as pH, ORP and DO. Performance was rated good based on the reduction of the contaminants. This does not necessarily mean reductions to target levels or MCLs.

Based on these methods, distribution of ZVI appeared to be good in 8 out of the 11 sites with sufficient data. Performance appeared to be good in 7 out of the 11 sites. Thus, the overall performance of this technology could be said to be fair, with uncertainty remaining.

7.7 CASE STUDY PERFORMANCE SUMMARY

This case study is located at Charleston Naval Complex, Solid Waste Management Unit (SWMU) 25, which is a former plating shop. The waste acids from historical plating operations were conveyed through a utility trench that allowed them to leach into groundwater. Vertical groundwater profiling was performed to define the locations with the highest concentrations of Cr(VI) in the groundwater; these data were then used to define the extent of the TTZ.

The geology at the SWMU-25 site consists of predominantly fine sands and sandy silts interbedded with sand to depths of 24 feet bgs. Thin plastic clay stringers have also been identified at depths greater than 15 feet bgs. An aquitard consisting of dense, dark olive silty clay is present at approximately 24 to 31 feet bgs. The remedial objective for the site was to

reduce Cr(VI) groundwater concentrations in the TTZ, which was approximately 150 feet by 150 feet in area, to less than 100 μg/L.

Pneumatic injections were performed within 16 boreholes between January 8 and 28, 2002. Figure 22 is a photo of the injection equipment. Each injection event consisted of a 5 to 15-second injection within a discrete 2-ft vertical interval in the borehole. Injections were performed starting at the deepest interval, working upwards in the borehole. Each interval was sealed using pneumatic packers that were inflated above the target injection zone. A lower straddle packer was not required, because the sandy formation collapsed below the injection equipment, as it was raised up the borehole, forming a boundary below the injection nozzle. A total of 16,725 kg (approximately 37,000 pounds) of ZVI was injected into the subsurface. This equated to a ZVI mass-to-soil mass ratio about 0.06% (assuming 100 pounds per cubic foot for media within the TTZ).

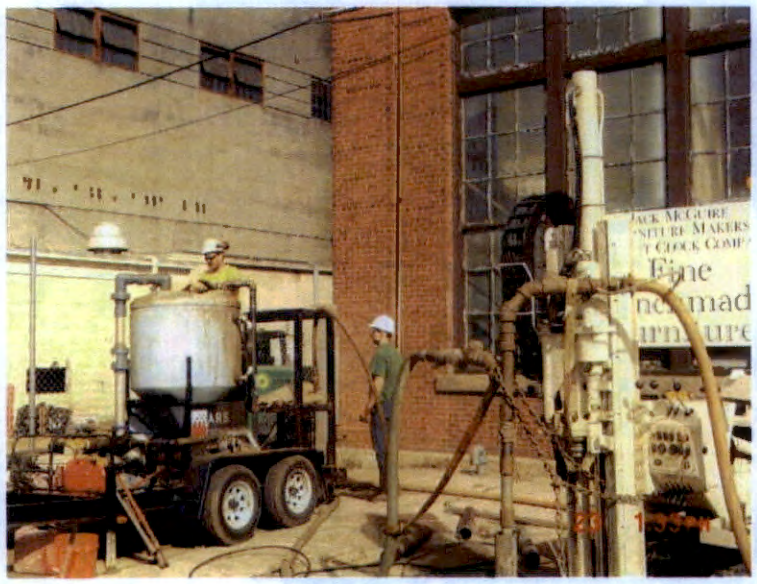


Figure 22. Pneumatic Injection Equipment at CNC SWMU25

Fracturing appeared to occur at depths deeper than approximately 15 feet. Above that depth the injection flow and pressure had to be limited to prevent surfacing of the ZVI slurry. Figure 23 is an illustration of the observed pressure response curve at one of the deeper injection points.

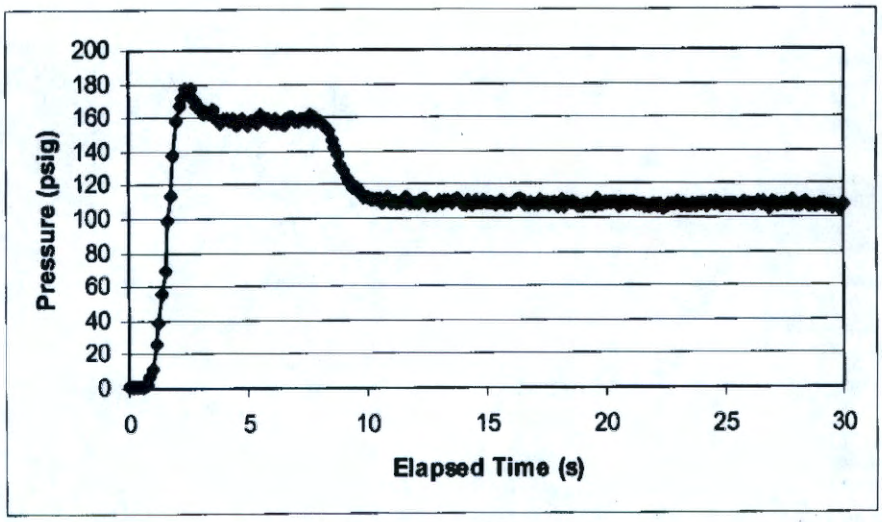


Figure 23. Typical Pressure Response Curve (23 to 25 feet bgs)

The performance of the injections in terms of Cr(VI) reduction are illustrated by the data from monitor well E070GW01D, which contained the highest pre-treatment Cr(VI) concentrations. Cr(VI) concentrations decreased rather rapidly from their pre-injection concentrations of around 30,000 µg/l (Figure 24). The rate of reduction slowed after approximately 3 years, when Cr(VI) concentrations had decreased to approximately 4,000 µg/l. However, concentrations have continued to decline and currently are ~700 µg/l, more than 6 years after the injections. Although reducing conditions persist at the site, an injection of lactate was recently performed in the most contaminated area to further reduce the concentrations in that area.

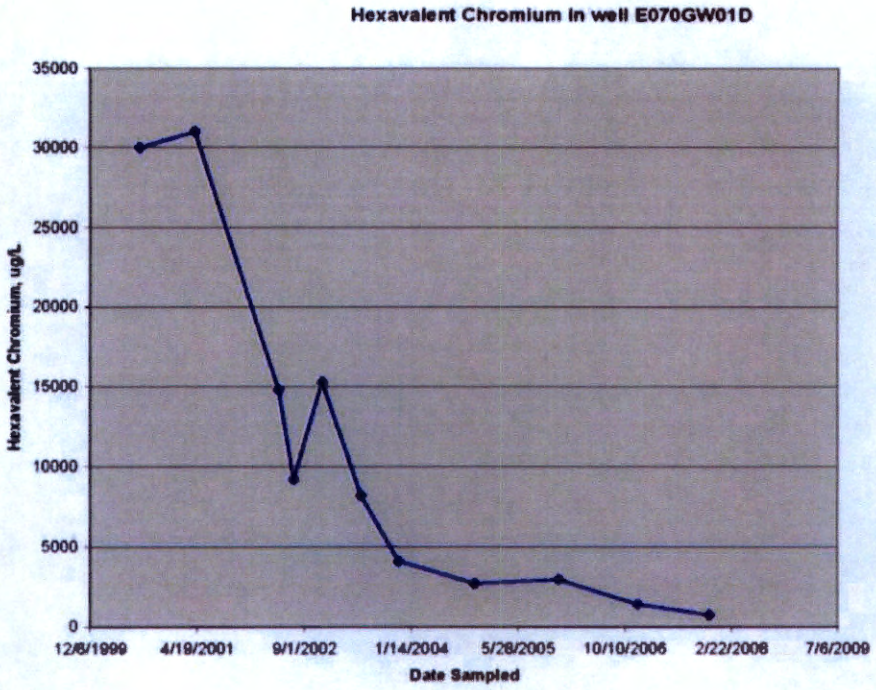


Figure 24. Cr(VI) Concentrations in Well E070GW01D over Time

8.0 SUMMARY OF THE HISTORY OF *IN-SITU* REDUCTION OF HEXAVALENT CHROMIUM USING CALCIUM POLYSULFIDE

By Jim Rouse, MWH Global Americas, Inc.

8.1 INTRODUCTION

Calcium polysulfide (CaS_x) has been used for *in-situ* reduction of Cr(VI) for more than 25 years at sites throughout the United States, as well as a few sites in Europe and Australia. This section presents the history of remediation activities in a few case studies. The studies demonstrate that there are two keys to the successful remediation of Cr(VI) via *in-situ* techniques:

- selection of the appropriate reductant based on the site geochemistry, and
- selection of the appropriate reagent delivery method based on site hydrogeologic conditions.

To achieve success, both of these factors must be successfully evaluated and the preferred methods must be designed based upon site specific conditions.

Even though Cr(VI) remediation has been ongoing since the early 1980's, much of this work draws on experience from the restoration of uranium *in-situ* leach mines in Texas and Wyoming in the 1970's and early 1980's. Uranium and chromium have similar geochemical behavior, and both are present in Hanford groundwater at concentrations that exceed background.

Early work on *in-situ* restoration involved the use of ferrous ions to directly reduce the uranium, producing a solid, relatively insoluble hydroxide precipitate; however, at some sites problems resulted from the decrease in permeability of the aquifer material due to the precipitation of ferric hydroxide. Because of these concerns, polysulfide material, most commonly CaS_x, was tested for its ability to promote reducing aquifer conditions. More recently, a finely ground ferrous sulfide slurry has also been applied at sites involving chromium ore-processing residue (COPR), because such COPR sites commonly contain groundwater containing Cr(VI) at levels in percent ranges and treatment of these sites with polysulfide has resulted in some rebound, as the Cr(VI) disseminates from the interior of the COPR particles over time after treatment.

With respect to the delivery method, site conditions play a major role. Successful remediation has involved percolation of reductant solution from the surface through pits, trenches, pipe grids, and other surficial distribution methods, as well as grid injection through temporary bores (GeoProbe™) or other vertical piping in both the saturated and unsaturated zones. At sites containing high permeability units, the most successful approach has involved pumping contaminated water from the central portion of the plume, treating it on the surface, and reintroducing the treated water either through injection wells or trenches around the margin of the plume and through infiltration basins in the former source area.

8.2 CASE STUDY: UNIVERSAL FOREST PRODUCTS, GRANGER, INDIANA.

This site, located immediately south of the Indiana-Michigan boundary in Granger, Indiana, was remediated under the oversight of the Voluntary Remediation Program of the Indiana Department of Environmental Protection. Remediation involved a total of four plumes on the site of this active Cr(VI) copper arsenate (CCA) wood-treating facility in the early 1980's.

8.2.1 Site Conditions

The four separate Cr(VI) plumes resulted from the surficial migration of CCA treating solution into the groundwater, which was located at a depth of approximately 10 feet. The site was underlain by approximately 70 feet of uniform fine to medium sand, deposited by glacial outwash streams. The site is located in an urban area, with individual water supply wells on the various lots, some of which were as close as the width of a street from the site. The site had previously undergone approximately 13 years of P&T efforts with little success. Subsequent investigation documented that a significant source of contamination was held in the unsaturated zone, serving to continually supply contaminants to the aquifer.

8.2.2 Approach

Remediation was accomplished by percolation of reductant solution using various methods, including an infiltration pipe grid in one area, an existing pond in another, a trench excavated across the plume in the third, and a series of injection wells in locations difficult to access in the fourth plume. Three of the plumes were treated using CaS_x, while the fourth was remediated using sodium metabisulfite, at the request of the client, who feared odor problems associated with CaS_x at the school that was located across the street from this plume.

8.2.3 Success

All four plumes were remediated to a level required by the Indiana Department of Environmental Protection, which subsequently issued a letter of "no further action." Since that time, more than 20 years of monitoring has demonstrated that the reduced Cr(III) has not remobilized or been converted to Cr(VI).

8.2.4 Lessons Learned

The only difficulty experienced at this site was associated with the formation of calcium carbonate crystals in the form of aragonite needles, which temporarily plugged the piping and led to the loss of process solution. This was corrected by using flexible hose in place of rigid pipes, allowing the crystals to break off as the hose was flexed.

The remediation of this site demonstrated that infiltration, through a number of different modes of delivery, is successful at remediating both the solid phase source of Cr(VI) contained in interstitial fluid in the unsaturated zone, and the dissolved Cr(VI) in the saturated zone. Much of this contamination was displaced from the unsaturated zone to the saturated zone in a plug flow mode, thereby requiring the capture using recovery wells within the area of infiltration.

8.2.5 Application to Hanford

The success at the Universal Forest Products site is directly applicable to the Hanford site, because a large source of Cr(VI) may likely remain in the interstitial fluids in the unsaturated zone, serving as a continuing source to the saturated zone. The use of infiltration as a delivery

mechanism to treat the unsaturated zone is believed to be an appropriate component of the overall remedial system for the chromium plumes at the Hanford site.

8.3 CASE STUDY: VALLEY WOOD PRESERVING, TURLOCK, CALIFORNIA

This was a former CCA wood-treating facility, no longer active. As a result of spills and seepage from the former plant site, a groundwater plume of Cr(VI), approximately 1/3 miles wide and 30 feet thick, extended approximately one mile down-gradient from the facility. At this site, the water table typically fluctuated five to eight feet over a year's period of time, due to infiltration of rainfall into the adjacent agricultural farmland. However, the plant site was largely paved with asphalt, except for an up-gradient area of infiltration basins, which had previously been used for more than a decade to support site P&T activities.

8.3.1 Site Conditions

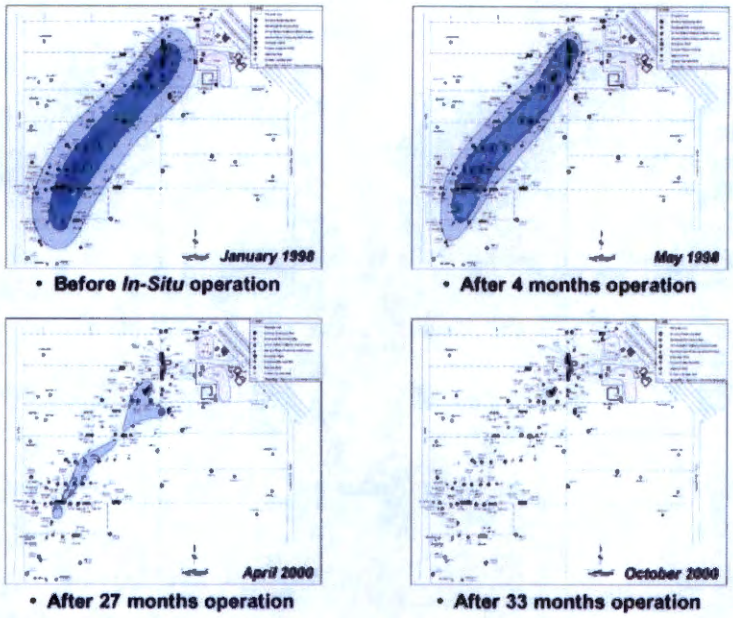
The Valley Wood Preserving (VWP) site and adjacent area is underlain by interbedded clay, silt, sand, and gravel deposits, deposited by runoff from the streams draining the Sierra Nevada Mountains to the east. Due to area-wide agricultural activities, the groundwater was highly contaminated with nitrate, and was saline, resulting in little or no use of the near-surface unconfined aquifer. More suitable groundwater was present at depths of approximately 200 feet bgs, beneath a thick clay aquitard. The prior decade of P&T activities had utilized a series of recovery wells located down the axis of the plume, pumping back to an electrochemical precipitation system, in which ferrous ions were added to the recovered water in excess of the amount needed to reduce the Cr(VI). The treated water was then discharged into a 330,000 gallon above-ground storage tank, where the resultant ferric hydroxide and chromium hydroxide settled out. Decant from the tank was then piped to the infiltration basins up-gradient of the former plant site.

8.3.2 *In Situ* Remedial Approach

Once a decision was made to utilize *in-situ* fixation, the EPA issued a ground-water pilot study (GPS) permit to allow *in situ* remediation efforts at the site. Treated water from the 330,000 gallon storage tank was dosed with CaS_x and injected in 23 wells located around the perimeter of the plume, where concentrations were equal to the MCL. Plans called for approximately 90 to 95 percent of the extracted water to be treated and then injected around the margin of the plume; the remaining 5 to 10 percent was to be pumped into the up-gradient infiltration basins. In this way, an *in situ* circulation system was created with a "hydraulic head minimum" down the central portion of the plume along its length with "hydraulic head maxima" around the margin of the plume, promoting flow of the injected water inward towards the extraction wells. After approximately six months, a second ring of injection wells was drilled closer to the core of the plume; the original injection wells were then abandoned, as the margin of the plume had shrunk. Addition of reductant to the treated water continued for approximately one year, after which only the treated effluent was injected while the extraction wells in the middle of the plume continued operation.

8.3.3 Success

The plume was essentially remediated to non-detect values in less than three years of operation. Results through time are shown on the four maps below in Figure 25.



• Before *In-Situ* operation
• After 4 months operation
• After 27 months operation
• After 33 months operation

Figure 25. Variations in Chromium Concentrations over Four Sampling Periods, Valley Wood Preserving Facility

The addition of CaS_x also eliminated the widespread nitrate contamination in the aquifer. However in local areas, the addition of CaS_x resulted in increased sulfate concentrations above the secondary drinking water standard in the unconfined aquifer. In addition, local areas of arsenic and manganese mobilization were detected. Such increases were limited in both spatial and temporal extent.

Because of elevated arsenic concentrations in the subsurface due to a spill of arsenic acid, it was not possible to add CaS_x to treat Cr(VI) to suitable levels in four wells on the plant site, because of concerns regarding arsenic mobilization. Therefore, nanoscale ferric hydrite slurry was injected in a grid pattern at those locations. Because the nanoscale ferric hydrite slurry also contained ferrous chloride, arsenic could be bound in a non-leachable form in the ferric hydrite particles. Within one week of the conclusion of the injection of the nanoscale ferric hydrite slurry, no detectable Cr(VI) or arsenic was present in the four wells. Subsequent monitoring for the next six months demonstrated long-term effectiveness of this approach.

8.3.4 Lessons Learned

The generation of reducing conditions during the remediation caused sulfate concentrations in the non-used aquifer to temporarily exceed the secondary drinking water standard for sulfate. Also, there was local and temporary exceedence of manganese and arsenic standards in some of the wells.

To prevent the production of excess sulfate as a result of CaS_x injection, a carbon source, such as corn syrup, molasses or ethanol, can be added to enhance the growth of sulfate-reducing

bacteria (SRB). Such SRB activity not only prevents increases in sulfate, but also provides additional benefits by promoting reducing conditions.

8.3.5 Application to Hanford

The delivery approach used at the VWP site, consisting of extracting from the core of the plume, treating the water with CaS_x and reinjecting around the margin of the plume, has direct applicability for several of the large, dilute Cr(VI) plumes at Hanford. Experience at the VWP site indicates that approximately 1.5 pore volumes of water would need to be pumped and reinjected to achieve Cr(VI) remediation.

8.4 CASE STUDY: CARTER HOLT HARVEY, MOUNT GAMBIER, SOUTH AUSTRALIA

The Mount Gambier CCA facility was originally constructed by the South Australian government to promote the timber industry in South Australia. Upon discovery of significant groundwater contamination from the operation, the South Australian government sold the site to Carter Holt Harvey, with the requirement that they remediate the contamination. This was done using *in situ* remediation, over approximately a three-year time period.

8.4.1 Site Conditions

The Mount Gambier site is underlain by cavernous coralline limestone, with numerous solution cavities, which generally trended at right angles to the direction of groundwater flow. The site was located approximately one kilometer up-gradient of the city water supply and major tourist attraction for the town of Mount Gambier, known as Blue Lake. The site was overseen by the South Australian EPA, which had never been involved in either an *in situ* remediation project nor monitored natural attenuation (MNA). Thus, significant effort was required in educating the regulatory body.

The water table was located at approximately 16 meters depth bgs. Above that, the coralline limestone was pierced by vertical solution cavities, filled with silt, on a spacing of approximately one per square meter area. These solution channels provided ideal pathways for vertical migration of contamination, but would have been very difficult to locate.

8.4.2 Approach

While the CCA plant was operating, an interim remedial measure consisted of pumping from the core of the plume, treating the water with CaS_x, and reinjecting the treated water through injection wells around the margin of the plume. After the plant was decommissioned, the drip pad, considered to be the main source of contamination, was excavated and replaced by an infiltration basin, filled with gravel. At that time, the treated water was largely returned to the infiltration basin, to allow the remedial solution to follow the same pathways as the original source of contamination. To aid in distribution of solution, a series of infiltration trenches were also constructed across the plume, and around the margin of the plume. These trenches were used to replace the infiltration wells, which experienced plugging. The remedial action continued for approximately two years, at which time the site met conditions established by the South Australian EPA for closure under a MNA approach. Monitoring has continued for five years, and a recent five-year review demonstrated that there has not been remobilization or off-site migration in excess of the South Australian EPA requirements.

8.4.3 Lessons Learned

The only difficulty experienced at the site was plugging of some of the injection wells, due to the high calcium content of the native groundwater and the CaS_x solution. This was overcome by switching to infiltration trenches and basins, which allowed precipitation of the calcium carbonate and elemental sulfur in the void space within the infiltration features. No significant remobilization or migration has been noted; temporary mobilization of arsenic and manganese has decreased.

The injection wells experienced some plugging difficulties, which this was overcome by switching to infiltration basins and trenches. Understanding of aquifer geochemistry is essential to appropriate design of the delivery system.

8.4.4 Application to Hanford

The use of infiltration basins and trenches for delivery of treatment solutions should be considered at the Hanford site in context with the unsaturated and saturated zone mineralogy and aquifer chemistry.

8.5 MARLEY COOLING TOWER COMPANY, STOCKTON, CALIFORNIA

The Marley Cooling Tower site was the one of the first locations where CaS_x was tested as an *in situ* remedial method in the early 1980s. While the test work proved positive, the client was unwilling to apply an unproven technology, and rather chose to install a P&T system, treating water via ion exchange before it was discharged to a surface water body under an NPDES permit. This P&T operation continued for almost 20 years before the new property owner elected to revisit the idea of *in situ* remediation. Such remediation consisted of three phases, described in the following sections.

8.5.1 Site Conditions

The site was used in the 1970's and 1980's for CCA treatment of timber to be used in construction of cooling towers. Contamination of the subsurface resulted from the installation of a series of "dry wells" under the retort vessel, to discharge contaminated water resulting from rainfall events. In addition, contamination also resulted from infiltration of concentrated CCA solution draining off of the "drip pad," and to a lesser extent, infiltration of contaminated storm water from a large storm-water holding pond located up-gradient of the retort facility. Contamination migrated horizontally and vertically downward through the interbedded sands, silts, clays, and gravel layers, and impacted water supply wells more than a mile down-gradient of the facility. The P&T system was successful in achieving hydraulic control and eliminating migration of the Cr(VI) contamination to the water-supply wells, but was not successful in restoration of the shallow contamination, both onsite and in the residential area down-gradient of the facility.

8.5.2 Approach

The *in-situ* approach chosen consisted of three phases. In the first phase, a single-point injection of diluted CaS_x and ethanol was injected into a central injection well, and the effect monitored in adjacent monitoring wells. This monitoring continued for approximately two years, while regulatory approval was obtained for the second and third phases. The two-year monitoring program allowed monitoring of the longevity of the reducing conditions generated

by the single injection, and provided data regarding the potential for mobilization of arsenic and manganese due to changing geochemical conditions.

The second phase consisted of multiple injection points, in both the shallow saturated zone and the underlying deeper zone, within the core of the plume. This injection grid was conducted just up-gradient of the Phase I test site, and spanned the width of the contaminant plume. It also extended up-gradient to immediately adjacent of the main source area, the wood-treating retort. Because of the presence of a RCRA cap over the prior area of the retort pit, no effort was made to remediate the contamination immediately underlying the pit. Monitoring the effect of Phase II injections demonstrated that the groundwater concentrations along the entire width of the plume were at non-detect values, as a result of the injection in the number of grid points, as shown below (Figure 26). The shaded area is at "less than detection" concentrations for Cr(VI).

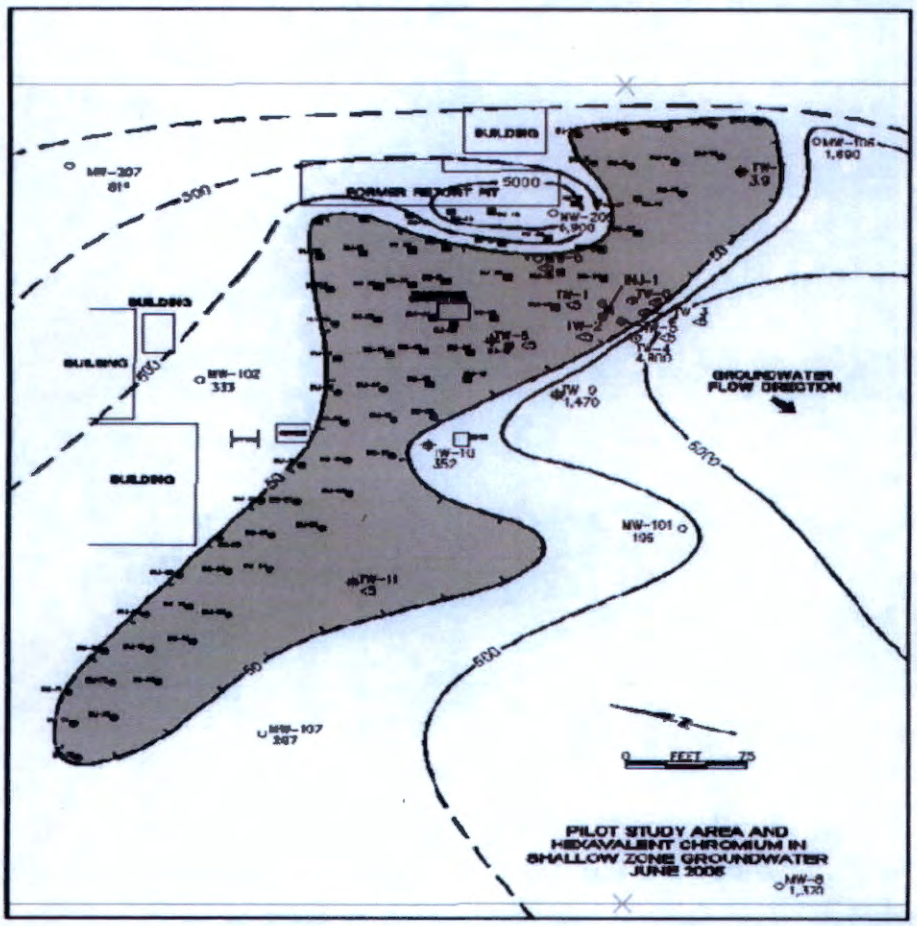


Figure 26. Post-Injection Chromium Concentrations Across the Pilot Study Area

Phase III, now underway, consists of emplacing a grid of injection wells across the area, to eliminate the source and the up-gradient portion of the contamination. In addition, a number of lines of injection points will be constructed in down-gradient areas, along the streets and alley ways in the residential area. Lines of injection points will also be placed in a school athletic field underlain by the plume. In addition, five horizontal wells were installed beneath the retort pit at a depth of approximately 15 feet to be used for the introduction of potable water to flush

mobile Cr(VI) out of the soil. Reductant will not be added to the lixiviant used in these wells, because of the presence of significant amounts of solid-phase arsenic, which would be mobilized by the introduction of reductant solution. A series of deeper horizontal wells installed under the retort pit below the arsenic source material, but above the water table, will be used for introduction of reductant solution to generate a reducing environment in the unsaturated zone to treat chromium displaced by the overlying soil flushing operation.

8.5.3 Success

The introduction of dilute polysulfide solution and ethanol by means of temporary bores to depths of more than 150 feet has proven highly successful. Monitoring of Phase I and Phase II has demonstrated that reduction of Cr(VI) is effective, while producing reducing condition that will last for a period of at least two years. By contrast, mobilization of arsenic and manganese, and increases in sulfate, are relatively temporal and not anticipated to migrate out of the immediate area of the reducing zone.

In the operational mode during Phase III, the solution was mixed into trailer-mounted tanks from a central mixing point, and transported via means of the trailer to the injection rig, which pumped the solution into the subsurface by means of a high-pressure pump at pressures sufficient to induce hydrofracturing. The trailer-mounted rigs will also be used in the streets and alleyways under the residential area, thereby minimizing disruption to the neighborhoods.

8.5.4 Lessons Learned

The previous P&T system, while effective in maintaining hydraulic control, did not remediate the subsurface. The prior consultant, who designed the P&T system, attempted to flush contamination from the retort pit area by injecting water in a series of vertical wells around the margin of the retort pit. This flushing was not successful, because the water tended to move vertically downward with little lateral spreading or contact with contamination in the retort pit area.

The prior work at the Marley Cooling Tower site demonstrated once again that the P&T approach, while potentially successful at maintaining hydraulic control, does not have a beneficial effect on the actual remediation of the subsurface. By contrast, a grid injection of dilute polysulfide solution and a carbon source is effective in remediating the contamination of the saturated zone, and in generating reducing conditions which last for at least two years.

8.5.5 Application to Hanford

Hanford currently operates a number of P&T systems. Just as in the case of the Marley site, such P&T systems will not be effective in remediating the aquifer, nor eliminating the source area in the unsaturated zone within a reasonable time period. P&T systems can easily be converted to *in-situ* treatment systems by utilizing the treated water effluent as a carrier for reductant into the subsurface, thus promoting much more rapid remediation. Testing at Marley and other sites indicate that such conversion commonly results in approximately 15 percent of the chromium remediated about ground and 85 percent remediated *in-situ*.

8.6 COAST WOOD PRESERVING, UKIAH, CALIFORNIA

The Coast Wood Preserving facility is an active CCA wood-treating facility, subject to the provisions of the Resource Conservation and Recovery Act (RCRA) which mandates that the "drip pads" for such facilities not be interrupted, under Subpart W regulations. This limitation, together with the fact that the site is active and is underlain by low permeability clays, in an area of extreme water-table fluctuation, has presented operational constraints on the use of *in-situ* techniques. Despite these constraints, the facility has essentially been remediated, while still in operation, thereby eliminating the need for large amounts of escrowed funds for closure of the plant site.

8.6.1 Site Conditions

During and immediately following the winter season, the water table is very close to, if not above, the land surface. The plant site is completely paved, and continues in operation as a wood treating facility, no longer utilizing CCA treatment solution. Assessment work has demonstrated that there were two separate groundwater plumes containing Cr(VI). One of these emanates from the wood-treating retort vessel area and is migrating under the drip pad to emerge on the down-gradient eastern side of the plant. The second plume had its origin in the area of a prior CCA solution spill, which migrated into the subsurface within a paleo-channel. The site operated a P&T system for more than a decade prior to switching to an *in-situ* remediation approach.

8.6.2 Approach

Because of the low-permeability conditions and the restricted access imposed by the activities on site, it was necessary to remediate the site by means of hydrofracture injection of reductant solution consisting of CaS_x and molasses. This injection was done via temporary GeoProbe™ boreholes, with the injection of concentrated CaS_x solution, followed by a "chaser" of water and molasses to distribute the polysulfide solution to some distance from the injection points. A total of five campaigns of such injections have been conducted to date.

8.6.3 Success

As a result of the five campaigns of grid injection, Cr(VI) concentrations underlying the Coast Wood Preserving facility have essentially dropped to non-detect. The only remaining area of contamination is immediately down-gradient of the drip pad area, where contaminants continue to migrate from under the pad in the groundwater and are measured in adjacent monitoring wells, before contacting reducing conditions. This localized contamination will probably remain until the plant is closed, when access under the drip pad is possible.

8.6.4 Lessons Learned

The greatest challenge within the Coast Wood Preserving facility is the inability to access the contamination under the drip pad, as a result of stringent RCRA regulations that preclude disruption of the drip pad.

A problem occurred during the initial attempt to introduce CaS_x solution in an existing trench up-gradient of the site. Because of the low permeability surficial materials, the polysulfide solution could not migrate from the trench unless high pressure was employed to hydrofracture the clay area.

The grid injection of concentrated CaS_x solution, followed by the introduction of water and molasses as a chaser, has proven highly effective at remediating low-permeability clay areas, even where the water table fluctuates widely. It has been demonstrated that such introduction should not be done during the high groundwater stages, as this tends to leave behind sulfide material in the unsaturated zone, resulting in formation of slightly acidic conditions.

8.6.5 Application to Hanford

In general, the approach taken at Coast Wood Preserving would not be applicable to much of the Hanford site, due to the much greater permeability of the subsurface materials at Hanford.

8.7 BOEING, LONG BEACH, CALIFORNIA

This Boeing facility is located on the north side of the Long Beach Airport, and is the location of prior construction of the DC-3 and C-47 aircraft by Donald Douglas before and during World War II. Two plumes of chromium contamination were present in the subsurface. The first of these resulted from a tank leakage at a former plating site, while the second resulted from more diffuse infiltration in the anodizing area within the manufacturing plant. Boeing desired to sell the property for residential and industrial development, and wanted to remediate the contamination as soon as possible, to permit the sale. This mandated a slightly different approach than would probably have been taken under other conditions.

8.7.1 Site Conditions

High concentrations of chromium were measured in the water table aquifer in the Shallow Bellflower Aquitard, which extends from the water table at a depth of approximately 50 feet, to approximately 80 feet bgs. Contamination was also present in the unsaturated zone in the two source areas. The subsurface consists of interbedded sands, silts, and clays in the unsaturated zone, and a silt aquitard in the first area of contamination. No significant contamination was noted under the Shallow Bellflower Aquitard.

8.7.2 Approach

For the bulk of the contaminant plume, injection through temporary boreholes placed by cone penetrometer or GeoProbe™ rigs was utilized for the delivery of a dilute reductant solution consisting of CaS_x, corn syrup, and potable water. The solutions were mixed at a central mixing plant and transported by 5,000 gallon tanker trucks to the injection points. For remediation in the former plating area, an infiltration basin was constructed, with four recovery wells designed to capture displaced Cr(VI) from the unsaturated zone, in the middle of the basin. The recovered water was treated with CaS_x, retained in a settling tank, and then discharged back into the gravel-filled infiltration basin. Because of low permeability in the upper material, a series of probe holes were subsequently placed in the upper five to ten feet of the basin. After this also proved unsuccessful, a total of six injection wells were drilled through around the margin of the infiltration basin within saturated materials.

Within the more diffuse source area, a tight grid of injection wells were placed, and injection proceeded from a depth of five feet and extending to the base of the Shallow Bellflower Aquitard.

8.7.3 Success

Remediation of the saturated zone was evident in a very short period of time, and, with the exception of a very localized area on the down-gradient portion of the plume, was successful at remediating the contamination throughout the site. Injection through the six wells ringing the basin was successful in the remediation of the saturated zone.

8.7.4 Lessons Learned

Infiltration in the former plating area was not successful at remediating the contamination of the unsaturated zone, due to the shallow low permeability and thin interbedded nature of the unsaturated zone. In a similar fashion, the unsaturated zone injection in the more diffuse portion of the plume was also not successful due to the inability to achieve a satisfactory distribution in the subsurface. Due to the short time period available prior to sale, Boeing elected to excavate the contaminated soil to a depth of approximately 15 feet and replace that material with clean soil, thereby assuring that future property owners would not have potential exposure to contaminants.

Delivery of treatment media using shallow injection or a surficial percolation basin in areas of extremely low permeability in the shallow subsurface is not an effective method of distributing the reductant solution throughout the unsaturated zone or the underlying aquifer. While it is true that when first contacting the subsurface, the contaminants followed a vertical pathway downwards from the surface source, such migration took many decades as opposed to the engineering infiltration, which was planned to be effective in a very short time prior to property sale.

8.7.5 Application to Hanford

This case study does not directly apply to the Hanford because the geology is starkly different, with very low permeability material present in the shallow subsurface, the opposite of Hanford conditions. Grid injection through temporary boreholes at Hanford would be challenging, but not impossible, because of the coarse-grained nature of the geologic materials.

8.8 SUMMARY

The following points summarize the application of CaS_x for remediation, while also discussing applicability to the Hanford site.

- Chemical reduction of Cr(VI) by CaS_x has been accomplished at several sites over the past 20+ years, in varied hydrogeological regimes. Addition of a carbon source prevents excess sulfate formation and allows the reducing effect to be longer lasting.
- Monitoring at these sites has shown that remobilization of chromium or transformation of chromium to the trivalent form is not a significant factor.
- The most effective delivery system for the reductant depends on site hydrogeologic conditions.
- Remediation can be accomplished in both the unsaturated and saturated zones; remediation of the saturated zone is typically easier to accomplish. Injection

through vertical boreholes in a grid pattern is not generally effective in low-permeability unsaturated zone material, but is effective in saturated conditions in such hydrogeologic regimes.

- P&T systems, while effective at maintaining hydraulic control, are not usually effective at remediating groundwater contamination; however, such systems can easily be converted to effective *in situ* remedial systems.

- Generation of reducing conditions, by chemical or biological systems, has the potential to cause temporary and local exceedances of arsenic and manganese concentrations, but these do not migrate from the area where reduction has been targeted.

This page intentionally left blank

9.0 *IN SITU* BIOREMEDIATION

By Jim Harrington, Alexco Resources, Inc.

9.1 HANFORD 100 AREA SITE-SPECIFIC ISSUES

The following is a summary of site-specific issues in the Hanford 100 Areas that affect the potential for bioremediation (many of these issues are likely to be issues also for other *in situ* reductive chromium treatment approaches).

- As-yet, source(s), i.e., residual unsaturated zone continuing contribution, is only partially known or unknown. Also the flux of water through the unsaturated zone is also unknown, as lysimeter data are not available, and even if it were, the interaction of unsaturated-zone water with the solid-phase chromium sources is a poorly understood process.

- The existing plumes are not-yet fully delineated (both lateral and vertical boundaries). It appears that the lateral location for the bulk of the mass is known for most of the plumes sufficiently to understand the scale of potential remedies, especially an interim remedy. However, better knowledge would typically be required to understand the level and type of effort required to obtain closure through implementation of a final remedy for these plumes.

- The "washing machine effect" of bank storage, both daily seasonal patterns, is not fully understood. This effect:

  - can influence re-oxidation of reduced byproducts of *in situ* reduction by introducing oxygenated river water into the groundwater near the river, making reduced iron or manganese less likely to reach the river. The oxygen in this water will then react with the iron and manganese, leading to the rapid formation of iron and manganese oxides. (Iron oxides and manganese oxides are also capable of sorbing dissolved Fe^{2+} and Mn^{2+}, which will substantially retard the transport of these secondary byproducts of a reduced zone formation toward the river even during times where oxygen is absent.)
  - influences travel time to the river, which should be understood for consideration of seasonal impacts on the remedial design (e.g., creation of reduced zones may be scheduled during periods of relatively longer travel time, followed by more rapid flow through the reduced zones during shorter-travel time seasons).
  - may decrease longevity of reduced zones by introducing oxygen (both by vertical water table variations, as well as by oxygenated water reaching the reduced zone). This likely makes the water-table fluctuation zone the weak point of any *in situ* remedy with respect to longevity of the reduced zone.

- Highly transmissive zones are abundantly present in the 100 Areas, which account for much of the Cr(VI) transport and which will accept the majority of the volume of any injected solutions. This will cause non-uniformity in the strength of the (solid phase) reduced zones.

- Less-transmissive zones, such as the thick Ringold Upper Mud and thin stringers within the upper units exist; the extent of these zones and their capability to adsorb Cr(VI), potentially re-releasing it at some time in the future, has not been determined. If this condition exists, final closure could be delayed. In my experience, this is not typically a significant issue in Cr(VI) sites, but this potential factor should always be kept in mind.

- The final cleanup standard of 10 or 20 μg/L affects the extent/coverage of a reduced zone and the sensitivity of continuing sources to affect closure of an area. In a case with ongoing unsaturated zone sources, it may be difficult to achieve concentrations of 10 or 20 μg/L Cr(VI) in nearby monitoring wells.

- Were a final cleanup standard lowered from 20 μg/L to 10 μg/L or less in a compliance well, the potential for α-MnO_2-caused re-oxidation of Cr(III) end-products of bioremediation becomes remote, but possible. The problematic scenario would likely only be observed in a zone where the influence of oxygenated water from bank storage could produce α-MnO_2 from adsorbed, reduced Mn^{2+}, while also oxidizing Cr(III) minerals to release dissolved Cr(VI). In the laboratory, this has only been shown to yield a Cr(VI) concentration of single-digit μg/L Cr(VI), and thus this possibility is considered remote at best.

- The presence of high concentrations (tens of mg/L) of nitrate-N in the aquifer significantly affects the stoichiometric demand of any reductant (CaS_x, organic carbon, ferrous iron) to create a reduced zone, and also affects the longevity of any barrier created. This likely was a factor in the predictions for the longevity of the dithionite-created barrier in the 100-D Area. A reduced zone created by injection of organic carbon will consume nitrate by microbial denitrification, which provides a secondary benefit toward the final closure of the 100 Areas by also remediating nitrate in groundwater.

- The presence of additional contaminants, such as radionuclides or other trace metals, could affect selection of an *in situ* treatment approach. The manner of this effect could include 1) consumption of reducing capacity, 2) potential concentration of a radionuclide in a barrier whether or not a reduced zone would be generated or emplaced in a barrier configuration, and 3) potential for non-specific consumption of reduced aqueous phases such as ferrous iron or sulfide by reaction with these metals. These other co-contaminants, if present, must be considered during the selection of the treatment approach and the monitoring program to ensure that the interim remedy is compatible with final closure requirements.

9.2 COMPARISON OF *IN SITU* TREATMENT REAGENT ALTERNATIVES

This section provides the author's opinion of comparable benefits and limitations of different reduced reactive zone approaches that were presented at the workshop.

9.2.1 Benefits

- Benefits of all *in situ* approaches are that the treatment reagent is delivered to the contaminant (Cr(VI)), rather than relying on extraction and treatment with the limitations of dilution and asymptotic cleanup efficiency. The author of this section

strongly favors plume-wide *in situ* treatment approaches, which are described below under the "proposed approaches" heading.

- Benefits of *in situ* reductive treatment include reduction of secondary contaminants such as nitrate and possibly other metals and radionuclides. As the presence and location of these secondary contaminants are not currently fully delineated, this statement is meant only to describe a potential benefit, the extent of which needs to be determined on a case-by-case basis.

- The timeframe to achieve complete cleanup is typically a few years when a plume-wide approach is employed, or a decade or two when multiple barriers are employed, whereas extract and treat approaches often can take multiple decades with decreasing efficiency over time. There is no technological limitation that would prevent plumes at the site from being completely treated in a few years if a plume-wide *in situ* treatment approach with a holistic strategy were to be employed.

- A very significant benefit of organic carbon-based reagents is their cost, which on a unit electron delivered (electrons being a unit of reduction potential) is *more than an order of magnitude less expensive than any other reagent.*

- Because organic carbon reagents are primarily not directly reactive with Cr(VI) and require a microbial action to directly reduce Cr(VI) or indirectly reduce Cr(VI) by ferrous iron or aqueous sulfide formation, transport of low levels of organic carbon can be efficiently done from widely spaced injection wells.

9.2.2 Limitations

- Limitations on ZVI as a reagent for reaction with Cr(VI) include:

  - the requirement to supply ZVI at a high-enough concentration in the aquifer solid phase to provide surface area for the ZVI-Cr(VI) reaction
  - relative cost of ZVI per unit of reducing power is higher than organic carbon-based reductants (methanol, ethanol, lactate, sugar syrups including corn syrup and molasses)
  - ZVI as a solid phase; consequently effective delivery into the aquifer is difficult; because it is a solid phase, its potential to surface passivate may also limit its longevity for continued reaction.

- Limitations on sulfide-based reductants (calcium, sodium, or hydrogen sulfide) include:

  - the high reactivity of these reagents with iron and other metal oxides affects the extent of delivery to the subsurface; where iron concentration in aquifer materials is high, the reagent-strength sulfide delivery is limited; this can be overcome with continued delivery of the sulfide reagent for a longer time, or by spacing the reagent delivery points closer, but ultimately this affects the cost and feasibility of sulfide-based reagents.
  - CaS_x has the least health and safety issues; the other forms are more complicated to deliver to the subsurface.

- The cost of sulfide reagents per unit reduction achieved in the subsurface is higher than organic carbon-based reductants.

- Limitations on the organic carbon-based reductants (methanol, ethanol, lactate, sugar solutions) include:
  - injection of a carbon source must be at high enough concentrations to deliver at reagent strength (defined as the concentration of a reagent that is sufficient to achieve treatment of Cr(VI) or formation of the desired reduced zone) at significant distance from the well; other electron acceptors including nitrate, iron, manganese, and sulfate will substantially affect the amount of the carbon source available to react with Cr(VI), and therefore the amount of carbon source required is far more than what is required based on Cr(VI) stoichiometric demand; the reduced minerals created from iron and sulfate reduction will provide a reduced zone to continue the reaction with Cr(VI); however, the longevity of these reactions has not yet been demonstrated to be longer than a few years.

- Limitations of any reductive *in situ* approach include:
  - generation of manganese, iron, and arsenic that may transport from the reduced zone toward the Columbia River; management of these secondary byproducts of *in situ* reduction can be accomplished by choosing the location of treatment at a sufficient distance to avoid migration of these secondary byproducts to the river, or by combining an *in situ* remedy with other remedial elements that would limit their migration. Two approaches could include combining *in situ* reductive treatment with a P&T system, or with an infiltration gallery injecting oxygen-saturated river water on the river bank between the *in situ* reduction system and the Columbia River.
  - delivery of the reagent into the subsurface; each reagent has its own challenges to delivering the required reagent strength within the aquifer, including:
    - delivery of reagents that limit disturbance is an objective that can impact both the selection of the reagent and the design of the delivery system; for instance, a reagent that can transport farther from an injection well than a comparable reagent will support a lower disturbance design because fewer wells will be required to achieve treatment.
    - loss during transport through the unsaturated zone is a variable that will affect whether the plume and the unsaturated zone can be treated by surface or near-surface infiltration systems, such as trenches, horizontal wells in the unsaturated zone, or infiltration ponds.
  - Selection of an *in situ* reduction reagent will be based on a wide range of variables in addition to those listed, such as safety, reliability, etc., but its ability to be delivered into the subsurface is an important one.

9.3 PROPOSED APPROACHES

9.3.1 Direct Injection with Treated Water

The water treatment systems currently employed at the site produce hundreds of gpm clean water that is currently re-injected into the subsurface outside of the plume areas. A complete

chemical and radiological analysis of the groundwater is strongly recommended before re-injection. The treated water should be viewed as a resource for creating *in situ* reduced zones. This approach was also recommended in Section 8.0.

As a point of illustration, consider injection of 100 gpm in a 50 foot thick aquifer through an injection well for 100 days. Assumptions include:

- reagent strength in the injection water is sufficient to create a reduced zone
- one hundred day groundwater transport time from the injection well
- radius of influence (ROI) from the injection well could be as large as 285 feet (0.15 flowing porosity assumed during injection); one injection well with these characteristics could directly treat nearly 2 acres of the plume.

It would not be required to directly treat the entire plume to achieve a rapid plume-wide cleanup. Lines of injection wells bisecting the plume would be used to create reduced zones that would then prevent Cr(VI) migration during up-gradient injection, allowing the down-gradient reduced zone to act as a "catcher's mitt" during the up-gradient injection time period. In this configuration, injection well lines spaced 1000 feet apart could be used to create reduced zones, then push up-gradient water into the down-gradient line. A water treatment system yielding 500 gpm of treated water could easily be used to create a single barrier up to 3000 feet wide every 100 days simply by directly re-injecting water with reagent back into the plume. A plume ½ mile wide by 1 mile long could be completely remediated this way in two years by placing five lines of five wells each, and sequentially injecting in the treatment lines with treated water amended with reagent. The displacement associated with the injection will tend to push the plume into the adjacent treatment lines, and natural groundwater movement will also carry clean water out of the treatment zones into the reduced zones, and carry Cr(VI)-contaminated water from the zones in-between the lines into the reduced zones. This example is given for illustrative purposes only, but is presented to show the rapid timeframes that could be achieved by utilizing the current P&T systems' treated water to eliminate plumes by re-injecting the treated water amended with a carbon source into the existing plumes.

9.3.2 Interaction of *In Situ* Remediation with a P&T System

The existing P&T systems create localized zones of more rapid groundwater transport toward the extraction wells. Temporary injection points or periodic injection into injection wells located in a ring around the extraction wells (a typical configuration would be 500 to 1000 feet out from the extraction well) can be used to rapidly clean up a volume of the plume, and should be considered as a way to rapidly treat the plume hotspots, such as the newly identified well containing approximately 40,000 µg/L of chromium.

One complication of a combined treatment system where extraction and treatment is paired with *in situ* reduction is the potential for secondary byproducts created by the reduced zone, which could include manganese, arsenic, and/or iron. If designed properly, the potential for high concentrations of manganese, arsenic, and iron in the influent water to the treatment system from the extraction well can be avoided. For example, if injection wells are spaced sufficiently far from an extraction well, the concentrations of these byproducts will be limited and may never exceed background, because they may be attenuated by a variety of mechanisms

during transport to the extraction wells. These mechanisms include dilution with non-flowing groundwater, sorption on iron and manganese oxides, precipitation with carbonate or hydroxide naturally present in groundwater, cation or anion exchange, re-oxidation with dissolved oxygen, nitrate, or ferric iron, and retention in/on microbial biofilms in the aquifer. Each site will have different aquifer conditions that control the potential for generation of secondary byproducts and their attenuation. If these byproducts are present in the extracted groundwater, an additional treatment step(s), such as an oxidation and filtration, may need to he added to the treatment system. However, the benefits of more rapidly treating the entire plume by combining remedies will be well worth the effort and added cost.

9.3.3 Recirculation Delivery Approaches

In general, two different recirculation approaches are currently being used to deliver organic carbon to Cr(VI) or other plumes for remedial purposes.

- Between-well circulation extracts water from one well, the water is amended with the treatment reagent, and the water is then re-injected into adjacent well(s), thus creating circulation cells; typically well screens are fully penetrating the zones where the contaminant occurs.

- In-well circulation extracts water from one screen and amends the water with the treatment reagent, and re-injects it in a second screen; in-well recirculation requires a blank non-screened well casing section and good well seals between the extraction and injection well screens to prevent short circuiting in the well bore.

    - Consequently, in-well circulation should not be considered for aquifers thinner than 30 feet, and are not ideal except for very thick aquifers approaching or exceeding 100 feet aquifer thickness.

    - When paired or placed in lines, the orientation (injection screen on top or bottom) is typically alternated to create a "conveyer-belt" result—adjacent injection and extraction screens are flow zones where groundwater primarily travels laterally to the adjacent extraction screen.

    - When the wells are spaced closely, vertical flow is minimized, and when they are placed near the limit of the influence of the adjacent well greater vertical flow is achieved.

Experience from other sites has involved spacing of recirculation wells greater than 100 feet and as broad as several hundred feet. The highly transmissive nature of the Hanford aquifer could make rapid recirculation and thus broader well spacing achievable. However, in many locations it is thinner than 30 feet. The carbon concentration in the recirculated water is controlled to have the carbon concentration at the extraction well remain low, and thus the half-life of the carbon source used will control the concentration in the injected water. As well spacing is broadened the carbon concentration required to maintain reagent strength is necessarily higher, and at some distance, the required reagent strength becomes the limiting factor. For planning purposes, a practical limit of 200 to 300 feet should be assumed.

9.3.4 *In Situ* Redox Manipulation Barrier Rehabilitation with Organic Carbon Recirculation Injections

The *in situ* redox manipulation barrier (ISRM) created by dithionite injection could be easily rehabilitated by organic carbon injection. A subset of the existing injection wells could be changed to be extraction wells, and paired injection well(s) would receive water from adjacent extraction well. The spacing of these recirculation pair(s) could be adjusted by selecting closer or more distant well pairs based on known transmissivity variability in the aquifer, with closer spacing for less transmissive zones. By recirculating for several months, reduced iron and sulfide will be generated in a pattern around the injection well. After several months, the extraction and injection well pairs would be flipped so that the reduced zone created around each injection well would then become overlapping. By creating a recirculation cell within the ISRM barrier, the width of the reduced zone could be greater than that achieved with the dithionite injections.

9.3.5 Injection Through the Unsaturated Zone by Infiltration

Areas with residual Cr(VI) can act as source areas if meteoric infiltration or leakage from water pipes allows for flow through the unsaturated zone and the infiltrated water encounters residual Cr(VI). The existing high-concentration plume areas are indicative of continued unsaturated zone sources. These areas could be remediated by infiltration of solutions with an organic carbon or sulfide reductant. Experience from other sites where the unsaturated zone was treated has shown that the leading front of the infiltrated solution mobilizes chromium, followed rapidly by the reductant, which effectively removes the contaminant, as evidenced in monitoring well or lysimeter data. The continued infiltration of organic carbon or sulfide reductant effectively remediates the primary flow paths, while residual deposits of reduced iron or sulfide formed from the reductant solution will support continued reduction of Cr(VI) if meteoric water or leaking pipes were to bring additional Cr(VI) to this location in the future.

For a thick plume, treatment of the whole footprint vertically is probably not feasible or efficient from a surface infiltration system. However, plume hotspots can be remediated by jointly combining injection or recirculation systems treating the water column, with an infiltration system. By first emplacing a down-gradient reduced zone, any Cr(VI) mobilized during the initial flush of the infiltration system will be treated.

9.3.6 Management of Reduced Secondary Byproducts Migration to the Columbia River

In general, any manganese, arsenic, or iron mobilized during *in situ* reduction will travel a short distance beyond the footprint of the reduced zone. However, because the chromium plumes are contiguous with the river, an effective approach may require creation of reduced zones near the river. The best method of managing the creation of secondary byproducts is by managing the concentration of organic carbon in the injection solutions, which limits the footprint of the reduced zone.

Where necessary, there are active management techniques that can prevent migration of these constituents toward the river. These approaches can be broadly classified as oxidation or hydraulic barriers, or a combination of the two. An oxygen barrier can be created by sparging oxygen, or by injecting oxygenated water in a barrier line. A hydraulic barrier can be created by injecting water and slowing or reversing the gradient toward the river. Both approaches

have been used to limit the migration of constituents such as the products of reduced zones near rivers.

9.3.7 Carbon Source Selection

The range of potential carbon sources is very broad; however, from a practical perspective, the economical carbon sources to be considered are limited to a few widely available carbon sources:

- Alcohols (methanol and ethanol)
- Organic acids (acetate and lactate)
- Sugar syrups (corn syrup and molasses)
- Vegetable oils

Alcohols have several advantages.

- are completely miscible with water
- are readily available
- are rapidly degrading
- have an antimicrobial effect in high concentration.

A reduced zone with alcohol is also geochemically simple, because complexation of metals with organic acids or fermentation products is not an issue, and there are only a few steps in the oxidation of alcohols to carbon dioxide. Alcohols are also relatively inexpensive on an electrons-delivered basis. Because alcohols are rapidly degrading (half-lives between 3 and 10 days is common) the edges of the reduced zone is sharp, and hence re-oxidation of reduced zone byproducts is also quicker, i.e., happens over a shorter distance.

Organic acids are already relatively oxidized compared to alcohols (average formal oxidation state of the carbon is positive vs. alcohols' formal oxidation state is negative). Consequently, even if these carbon sources were equivalent cost per unit weight or volume, they are relatively weak to create a reduced zone. Lactate is relatively more reduced compared to acetate, and is preferable as a result. Lactate half-lives are between 4 and 15 days. Acetate is a very poor carbon source and should not be considered unless it is the only carbon source available.

Sugar syrups are common agricultural byproducts and consequently are inexpensive and are in many cases an ideal carbon source to create a reduced zone. However, they typically are degraded by fermentation, and have a complex degradation route with many byproducts, some of which may complex metals. While their cost may be comparable with alcohols, the complexity of their degradation makes their usage in reduced systems a little bit more complicated than an alcohol. Their half-lives are also longer than shorter carbon chain carbon sources—from 15 to 40 days. The edges of the reduced zone is a little less sharp than alcohols as a result, and when bigger reduced zones from a single injection well is desired, use of sugar

syrups is ideal because the carbon compounds from the degradation of sugar syrups will stick around longer. These compounds have been widely used and consequently a broad knowledge base of experience is available.

Vegetable oils are good carbon sources, because they are strongly reduced and can be used as a slow-release carbon source. However, because they are immiscible with water, even emulsions of oils rapidly sorb onto aquifer materials, and hence delivery from an injection well is limited to a few feet around the injection well. In an aquifer such as Hanford where the thickness of the aquifer is significant and the cost of each individual well is great, the usefulness of oils is limited.

9.4 SUMMARY

In situ reduction using carbon sources is a very cost-effective way to create reduced zones. The most significant variable that affects the method of application of this technology is the delivery approach. In source areas, infiltration of carbon-amended water from the surface is a technology that can rapidly expedite closure. Injection of treated water amended with organic carbon from the existing P&T systems into wells is an approach that could be readily implemented, maximizing the existing infrastructure. Recirculation wells is an excellent carbon source delivery system in a barrier or plume-wide approach, and may be compatible with the aquifer at Hanford. Proper design and application of a combination of *in situ* reduction and delivery techniques is recommended to rapidly remediate the chromium plumes in the 100 Areas at Hanford.

10.0 TWO *IN SITU* REMEDIATION CASE STUDIES FOR TREATMENT OF CHROMIUM IN GROUNDWATER

By Ernie Stine, Shaw Environmental and Infrastructure, Inc.

During the workshop, this presentation included discussion on the basic chemistry of chromium, its oxidation states, conversion between the two major oxidation states (III and IV), how the chemistry affects the remediation of Cr(VI), general processes used to remediate Cr(VI), and two case studies *in situ* biological treatment and *in situ* chemical treatment.

10.1 INTRODUCTION AND CHEMISTRY

10.1.1 Chemistry

Chromium is a common contaminant in soils and groundwater. After lead, chromium is the second most common metal of concern at Superfund sites that have signed a ROD. The third most common metal is arsenic. Cr(VI) has been used as a corrosion inhibitor, e.g., in cooling towers, and in paint pigments, chrome plating, leather tanning, wood preservation, anodizing aluminum, and is present in refractory materials. Section 2.0 provides more detail on chromium speciation and oxidation/reduction chemistry.

Chromium mobility is dependent on its speciation, solubility in water, soil moisture content, and presences of other carrying fluid. The pH and oxidation-reduction potential (ORP) are the two quantifiable parameters commonly used to qualitatively determine the chromium speciation in the field.

High pH and high sulfate, carbonate, and phosphate concentrations increase the mobility of hexavalent chromium. In contrast, Cr(III) as the hydroxide is much less mobile. If Cr(III) precipitates in the presence of ferric iron, it forms a precipitate that has lower solubility than $Cr(OH)_3$. In addition, Cr(III) hydroxides can react with minerals containing ferric iron to produce low solubility and mobility iron-chromium-hydroxide species on and within the soil particles. As a solid or adsorbed species on the soil particles, Cr(III) can persist in the neutral and basic environments, and generally will not re-oxidize even in the presence of free oxygen (US EPA, 1994; US EPA, 2000; Hafiz, 2004).

In the laboratory, it has been shown that more soluble forms of Cr(III), e.g., citrate chelated Cr(III), can react with the freshly created amorphous forms of MnO_2. Manganese dioxide acts as a catalyst to oxidize chromium in this reaction. Oxygen from the air can then re-create MnO_2 to oxidize more Cr(III). This phenomenon has not been demonstrated to take place under normal environmental conditions (US EPA, 1994).

10.1.2 Remedial Concept

Cr(VI) can be removed from the groundwater by naturally occurring processes. One of these involves the reduction of highly soluble Cr(VI) to nearly insoluble Cr(III). As a result, Cr(III) will be precipitated on aquifer solids, resulting in reduced groundwater concentrations and reduced risk. Therefore, the typical approach for remediation of environmental sites is the *in situ* application of chemical or biological processes to reduce Cr(VI) to the less mobile Cr(III).

Reduction of Cr(VI) can occur through abiotic processes, for which naturally occurring reducing agents are used. It can also be catalyzed by bacteria, which use natural carbon sources as electron donors. These processes contribute to the natural attenuation of Cr(VI). The biological reduction of Cr(VI) with concomitant precipitation can also be enhanced by the addition of carbon sources to the groundwater, which serve as electron donors.

10.2 GROUNDWATER CHROMIUM TREATMENT STANDARDS

Groundwater Cr(VI) treatment standards vary between by state and federal governments. The trend is that treatment standards will continue to tighten. A few of the treatment standards are listed below, most are for total [Cr(VI) + Cr(III)] chromium.

Table 6. Treatment Standards in the United States

Location or Organization	Standard (µg/L)
USEPA MCL	100 Total Chromium
California	50 Total Chromium
Washington	80 Total Chromium
Virginia	50 Total Chromium
Texas	100 Total Chromium
Massachusetts	100 Total Chromium, Cr(III) and Cr(VI)
New York	50 Total Chromium and Cr(VI)
Hanford DOE Site	10 and 20 Total Chromium

There are five in-situ treatment processes typically used for *in situ* treatment of Cr(VI) in groundwater.

- Natural Attenuation
- Pump and Treat
- PRB's
- Chemical Reduction
- Biological Reduction.

10.2.1 Natural Attenuation

In some circumstances, Cr(VI) can be remediated by natural reductants in soil and aquifers, which can transform Cr(VI) to Cr(III), i.e., natural attenuation. This process relies on the anion exchange reaction with soil and naturally occurring electrochemical reduction of Cr(VI) to precipitate the chromium as a nearly insoluble hydroxide. For natural attenuation to be considered a viable option, then ideally it would be demonstrated that (US EPA, 1994):

1. there are natural reductants present within the aquifer

2. the amount of Cr(VI) and other reactive constituents does not exceed the capacity of the aquifer to reduce them

3. the time scale required to achieve the reduction of Cr(VI) to the target concentration is less than the time scale for the transport of the aqueous Cr(VI) from source area to the point of compliance

4. the Cr(III) will remain immobile

5. there is no net oxidation of Cr(III) to Cr(VI).

It is reasonably easy to meet items 1, 4 and 5; however, it may be difficult to meet items 2 and 3. As a result, from a regulatory basis, it may be difficult to rely exclusively on natural attenuation to remediate a chromium-contaminated site.

10.2.2 Conventional Pump and Treat

Historically, remediation of chromium-contaminated soils has relied on excavation/encapsulation or chemical reduction/stabilization. Groundwater was treated using P&T technology. P&T processes extract contaminated groundwater and treat the groundwater to meet discharge requirements. P&T systems are effective at hydraulic control and have been shown to significantly lower the concentration of chromium in groundwater. The disadvantage, however, is that it normally takes many years to meet the remedial goals, and consequently, it is one of the more expensive options for site remediation.

Cr(VI) is often removed from the extracted water either by adsorption or chemical reduction/settling/filtration processes. Absorption processes typically used anion exchange resins or zeolites. Cr(VI) is transferred from the water to the solid phase, thus purifying the water. The loaded adsorbents are either disposed or regenerated. Spent adsorbent needs to be characterized before disposal to determine if it is a hazardous waste. Disposal of spent regenerant solution may be problematic and expensive.

This section of the report focuses on the *in situ* processes used to treat Cr(VI) so it is mostly or totally removed from the groundwater *while below ground*, as well as reducing chromium toxicity. *In situ* treatment of Cr(VI) is typically accomplished by alteration of the oxidation-reduction state of the contaminated aquifer. This can be accomplished by chemical and/or biological reduction. Chemical fixation, or abiotic reduction, is accomplished by injection and distribution of a chemical reductant. Biological reduction is accomplished by injection and distribution of a biodegradable substrate, which when consumed by indigenous organisms creates reducing conditions, which then favor the reduction of Cr(VI). The goal of chemical reduction or fixation of Cr(VI) is to reduce it to stable Cr(III), which will precipitate or fix onto aquifer solids.

10.2.3 Chemical Reduction of Cr(VI)

Various reductants including metallic iron, ferrous sulfate, calcium polysulfide, and metabisulfite are available (Palmer and Wittbrodt, 1991). General reactions for reduction of Cr(VI) by iron (ferrous sulfate, ferrous chloride and metallic iron) include the following. In

these and other equations, the chromium species is written as Cr^{3+} for ease of interpretation. At normal groundwater pH values, Cr^{3+} would precipitate as the appropriate chromium hydroxide.

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7\ H_2O \text{ (acidic conditions)} \quad [19]$$

$$CrO_4^{2-} + 3Fe^{2+} + 4H2O \rightarrow Cr^{3+} + 3Fe^{3+} + 8OH^- \text{ (neutral or alkaline)} \quad [20]$$

$$CrO_4^{2-} + Fe^0 + 8H^+ \rightarrow Fe^{3+} + Cr^{3+} + 4H2O. \quad [21]$$

Abiotic reduction of Cr(VI) has been accomplished using ZVI, which has also been utilized successfully for several years as a treatment reagent for chlorinated ethenes. As with other reductants, ZVI treats contaminants by creating conditions where relatively oxidized compounds, such as tetrachloroethene (PCE) and Cr(VI), are reduced to less toxic products, ethene and Cr(III), respectively. Several distribution processes have been utilized for emplacement of the ZVI, including high-pressure injection of micron- and nano-scale particles and permeable reactive barriers using granular particles.

The applications of solid metallic iron and dissolve ferrous iron a shown in equations 19-21, have been successfully applied to treat Cr(VI). As with all in-situ techniques, care needs to be taken to understand the hydrology and groundwater flow patterns to be successful. Addition of ferrous salts has the potential of plugging the aquifer or injection points as iron oxyhydroxides may precipitate, making treatment less effective. The dimensions and structure of any PRB needs to be designed and constructed such that it maintains an effective residence time and the reactive media do not deactivate before all of the contaminant concentrations are lowered to the performance standard for the duration of the project. PRBs also need to be designed to ensure that they do not short-circuit or plug too much before the end of the project.

Sulfur compounds have also been used to treat Cr(VI). Several of these compounds and some of their generalized chemical reactions are listed below.

- Calcium polysulfide (CaS_4)

$$2CrO_4^{2-} + 3CaS_4 + 10H^+ \rightarrow 2Cr(OH)_3 + 12S^0 + 3Ca^{2+} + 2H_2O \quad [22]$$

- Sulfite (HSO_3^-)

$$7H^+ + 2CrO_4^{2-} + 3HSO_3^- \text{ (excess)} \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 5H_2O \quad [23]$$

- Metabisulfite ($S_2O_5^{2-}$)

$$S_2O_5^{2-} + H_2O \rightarrow 2HSO_3^- \quad [24]$$

$$7H^+ + 2CrO_4^{2-} + 3HSO_3^- \text{ (excess)} \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 5H_2O \quad [25]$$

$$S_2O_5^{2-} + 1/2O_2 \rightarrow S_2O_6^{2-},\ S_2O_5^{2-} + 2H+ \rightarrow 2SO_2 + H_2O \quad [26]$$

- Sodium Sulfide (NaS)

- Hydrogen sulfide (H_2S)
- Hydrazine (N_2H_2)
- Dithionite ($S_2O_4^{2-}$) and
- Fe-S compounds (slow to react with Cr(VI)).

A potential issue with several of the sulfur compounds, e.g., sulfite, metabisulfite and dithionite, is that SO_2 can be released if the pH becomes too acidic. There are significant health and safety issues with deployment of hydrogen sulfide and hydrazine.

10.2.4 Biological Reduction

Biological reduction of Cr(VI) to Cr(III) is accomplished by the injection and distribution of an easily biodegradable substrate into the contaminated aquifer. Common substrates include, but not limited to the following.

- Acetate
- Molasses
- Cow manure
- Fruit juice
- Lactate
- Whey
- Polylactate and sulfur-containing products, e.g., Metals Remediation Compound (MRC™)
- Waste organic material, e.g., from beer manufacturing (Perlmutter, 2001, Henny, 2001, Gemeots, 2003).

The indigenous organisms utilize the substrate as a carbon source for biomass generation and as an electron donor for energy production. Cr(VI) is a highly oxidized compound and therefore can act as an electron acceptor. The biological processes that can result in Cr(VI) reduction are summarized as follows:

1. Cr(VI) reduction via co-metabolism under aerobic conditions. This process is thought to be a detoxification mechanism where microorganisms produce a soluble enzyme to reduce Cr(VI) to Cr(III) (McLean and Beveridge, 2001)
2. Anaerobic reduction through the use of Cr(VI) as a terminal electron acceptor during anaerobic respiration (Lovley, 1993). This process is preferred, because respiration mechanisms are linked to growth and are therefore more sustainable than co-metabolic reactions.

3. Indirect biological Cr(VI) reduction resulting from reactions with reduced anaerobic respiration products, in particular ferrous iron and hydrogen sulfide. If Cr(VI) is present under iron reducing and sulfate reducing conditions, this process is almost inevitable, because Cr(VI) is too oxidized to be stable under such reducing conditions. However, as discussed below, it is not necessary to establish highly reducing conditions to electrochemically reduce Cr(VI).

Gemoets, et al. (2003) compared several molasses sources to lactate for bioreduction/precipitation of Cr(VI). Extensive removal of chromium from the groundwater by precipitation was only achieved for a limited number of conditions. In general, lactate was found to be the most effective carbon source. The results showed the removal of chromium from groundwater was less effective using higher concentrations of molasses, although the molasses addition caused a steeper decline in the redox potential. Significantly, Gemoets identified that the degree of Cr(VI) removal inversely correlated with the concentration of molasses. Phifer et al. (2003) confirmed that lactate was an effective substrate for creating sulfate-reducing conditions for the purpose of metals removal from the aquifer at the Savannah River Site. The use of lactate as a substrate in conjunction with ZVI was also used to reduce Cr(VI).

Perlmutter (2001) determined that molasses was a better substrate than acetate, cow manure, or fruit juice for Cr(VI) reduction. Molasses was recommended at that site, because of the lower substrate cost in comparison to acetate. However, results indicated that acetate may be needed to initiate the treatment system and that molasses may be effective as a long-term donor. Perlmutter also indicated that no special consortia of microorganisms were required for inoculation of the subsurface for *in situ* treatment. A possible advantage of molasses is that it contains additional sulfur. This sulfur may be available for the precipitation of additional Cr(VI) and other metals such as arsenic. Synthetic substrates such as MRC™ are being developed for in-situ treatment of metals. Biodegradable esters or salts of organosulfur compounds (including amino acids and other types of organic acids) can be synthesized into materials suitable for injection into the subsurface.

The ease of biological or chemical reduction of Cr(VI) is expected based on the following list of half-cell reactions where Cr(VI) has a more favorable reduction potential than nitrate, manganese dioxide, ferric iron, and sulfate.

Chromium Reduction
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ ($E_h^0 = {}^+1330$ mV) [27]

Oxygen (O_2) Reduction
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ($E_h^0 = {}^+820$ mV) [28]

Nitrate (NO_3) Reduction
$2NO_3^- + 12H^+ 10e \rightarrow N_{2(gas)} + 6H_2O$ ($E_h^0 = {}^+740$ mV) [29]

Arsenic (As) Reduction
$H_3AsO_4 + H_3AsO_4 + 2H^+ + 2e^- \rightarrow H_3AsO_3 + H_2O$ ($E_h^0 = {}^+559$ mV) [30]

Manganese (Mn) Reduction
$MnO2_{(s)} + HCO_3 + 3H^+ + 3e^- \rightarrow MnCO_{3(s)} + 2H_2O$ ($E_h^0 = {}^+520$ mV) [31]

Iron (Fe) Reduction

$FeOOH_{(s)} + HCO_3 + 2H^+ + e^- \rightarrow FeCO_3 + 2H_2O$ ($E_h^0 = {}^-50$ mV) [32]

Sulfate (SO_4) Reduction

$SO_4^{2-} + 9H^+ + 6e^- \rightarrow HS^- + 4H_2O$ ($E_h^0 = {}^-220$ mV) [33]

Carbon Dioxide (CO_2) Reduction (methanogenesis)

$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_20^-$ ($E_h^0 = {}^-240$ mV) [34]

10.3 CASE STUDIES

Two cases studies are discussed below. The Selma site used biological treatment and the Ecodyne project used CaS_x chemical treatment. Both sites were using conventional P&T remediation prior to implementation of these electrochemical reductive treatments.

10.3.1 Selma Pressure Treating Superfund Site

Shaw was contracted by the U.S. Army Corps of Engineers to perform groundwater remediation and cleanup activities at the Selma Pressure Treating Superfund site on behalf of the EPA, Region 9, San Francisco. Located in Fresno County, California, the 18-acre primary site is approximately 15 miles south of the City of Fresno and has recently been zoned into the city limits of Selma.

The site was operated from 1933 to 1990 as a wood treating facility. Consequentially the contaminants released to the groundwater include pentachlorophenol, arsenic, total chromium and Cr(VI), and copper. Chromium is the only contaminant detected in the groundwater at levels that exceed the MCL. The range of chromium detected in the groundwater varies from approximately 80,000 µg/L to below the detection limit. By 1997, the Cr(VI) plume had migrated some 3000 feet down-gradient from the primary site, reaching the unconfined aquifer under sensitive vineyards and farmland. The ROD for groundwater remediation specified P&T of the contaminated groundwater plume. The primary goals of the project were to 1) recover the contaminants 2) prevent further migration and contain the plume, and 3) protect potential receptors (local residential and irrigation wells).

Initially, an 8-well extraction system and a chromium reduction/precipitation process using ferrous chloride was designed, constructed, and operated to pump and treat 200 gpm continuously. Because the contaminant plume is bisected by California State Highway 99, permits were obtained from California Department of Transportation to install a boring under Highway 99 to transport the water from the down-gradient areas of the plume back to the primary site where the treatment plant was constructed.

Given the length and breadth of the plume, the treatment plant was projected to operate in excess of 30 years. A detailed evaluation of *in situ* and *ex situ* treatment options for the site determined that *in-situ* biological reduction of Cr(VI) would be a cost-effective option to treat the groundwater in less than 30 years.

A bench-scale study evaluating three substrates [EHC™ {a commercial proprietary ZVI/carbon blend}, molasses, and lactate] was completed before proceeding to the field. Each substrate was investigated in triplicate. The key findings from the bench study follow.

- Under current site conditions, intrinsic biodegradation of Cr(VI) is not occurring, most likely due to the absence of a carbon and energy source.

- Molasses significantly reduced Cr(VI) concentration faster than lactate and is a less expensive substate. This is contrary to common expectation and supports the need to do bench-scale testing before selecting a substrate.

- Biologically induced Cr(VI) reduction in the presence of molasses can occur under aerobic conditions and prior to induction of nitrate, iron, or sulfate reduction. Cr(VI) was likely being utilized as the terminal electron acceptor.

- Various formulations of EHC are viable remediation compounds to induce chemical and biological reduction of Cr(VI). EHC reduced Cr(VI) concentrations faster than molasses or lactate; however, the cost for treatment at this site would be higher using the specialized substrate.

- A change in the geochemical conditions from anaerobic to aerobic did not result in the generation of Cr(VI) species through oxidation of the reduced Cr(III) species. In the bench-study, after Cr(VI) was biologically reduced, the reaction vessel was removed from the glove box and air injected into the vessel for two weeks to drive the system to a highly aerobic condition. The vessel was sampled for Cr(VI); there was no Cr(VI) detected in the groundwater.

Similar to the bench-scale tests results, during the subsequent pilot-scale demonstrations described below, Cr(VI) reduction was initiated before nitrate reduction.

Site treatment was conducted in several phases. Phases 1, 1a, 2, and 2a used direct-push technology to inject molasses into the subsurface. Phase 1 injected molasses into the hotspot area. Phases 1a and 2 injected substrate in areas adjacent to the hot spot and down gradient of the hotspot, respectively. The injection field was based on a 15 ft radius-of-injection plan. In most cases, there was no overlap of the 15 ft ROI circles. Solutions of less than 5 percent molasses were injected at about 90 to 180 psi to meet an approximate a 4000 mg/L molasses target concentration. This concentration of substrate was an overdose amount with a 5X safety factor.

For Phases 1, 1a, and 2, treatment depths were up to 120 feet. Direct push was used to ensure that enough substrate was added to treat the high Cr(VI) concentrations. The ORP decreased from aerobic to zero or negative millivolt (mV) values within 10 to 20 days in all wells within the treatment area. Both total and Cr(VI) concentrations decreased soon after substrate addition. The decrease in total chromium groundwater concentration lagged behind Cr(VI) concentration decrease. This delay in total chromium removal is the time it took for the Cr(III) hydroxides to finish adhering themselves to the soil particles. Cr(VI) was reduced to less than the performance standard (50 µg/L) and in most cases to below 10 ppb. Overdosing with substrate resulted in establishment of excessively reducing conditions, which resulted in mobilization of some metals, such as iron (Fe^{2+}) and manganese (Mn^{2+}). As the site is returning toward its natural aerobic condition, the concentrations of these two metals are decreasing as they are oxidized, forming low-solubility metal oxides/hydroxides.

Even in areas where the total organic carbon did not increase much, i.e., the substrate concentration was low, Cr(VI) was effectively reduced. This is consistent with the bench-scale tests that showed that Cr(VI) can be reduced under aerobic and mildly reducing conditions.

Direct push technology is excellent for treating areas of high concentrations, e.g., source areas where the depth is less than about 110 ft. Excess dosing of reagent may lead to biofouling in the wells and distribution piping. The soil type, hydrology and permeability limit the radius-of-influence, e.g., 10 to 25 ft. As the radius of influence decreases, the number of injections will correspondingly increase.

Phase 2b was located further down-gradient. Because the plume was further away from the source area and deeper below ground, a recirculation process was used to add lactate. This treatment was redesigned from the Phases 1, 1a, and 2 to allow for lower substrate doses and treatment depths greater than 120 ft. The recirculation system distributed substrate throughout the treatment area by extraction of groundwater from radially arranged extraction wells (5 wells) and injection of water into centrally located injection wells (11 wells). The extraction wells were placed up-gradient, between and down-gradient of the injection wells. The substrate was changed from fast acting molasses to slower degrading lactate. Substrate was delivered to the recirculation system by regularly timed pulsed injections.

Field tests were conducted to determine the optimal amount of substrate required for the reduction of Cr(VI), thereby minimizing the establishment of excessively reducing conditions. The combination of using lower substrate concentrations, change in substrate and using a recirculation system controlled reduction in ORP and stopped biofouling.

Generally, the price to treat a site using such a recirculation system would range from $400 K to 1 million dollars. The price for direct push treatment is mostly driven by the number of injection points and the depth of treatment.

10.3.2 Ecodyne

Years of using chromium-containing preserving solutions at a former California wood preserving site led to high concentrations of Cr(VI) in soil and groundwater. A state agency-required environmental site assessment revealed as much as 6,000 pounds of Cr(VI) were present. To comply with a Cleanup and Abatement Order under the Regional Water Quality Control Board (RWQCB) and California Department of Toxic Substances Control (DTSC), a groundwater extraction treatment and reinjection system was designed, constructed, and operated. In its first 2 years of operation, the P&T system treated nearly 9 million gallons of water to recover about half of the hexavalent chromium. Recovering the remaining 3,000 pounds would have required another 10 years of operation.

Recognizing the high cost of operating the system for another 10 years, the consultant approached the customer with a cost- and time-saving alternative, *in-situ* geochemical fixation of metals. A pilot test, using CaS_x, demonstrated *in situ* treatment of Cr(VI) in soil and groundwater. CaS_x was added above groundwater to reduce the Cr(VI) to below 50 μg/L. This treated groundwater was reinjected into the subsurface through infiltration galleries and injection wells at the plume's source area. Results indicated *in-situ* geochemical fixation would clean up the site in 2 years. The project team presented these results to regulators and

successfully negotiated an amended Cleanup and Abatement Order to accommodate the alternative remedy.

Because the *in-situ* treatment system was similar in system design to the originally installed P&T system, the existing equipment, tanks, and piping could be adapted for the new application to reduce new equipment needs. The *in-situ* system completed the cleanup in only two years, reducing the life-cycle costs by $2 million.

10.4 TECHNOLOGY IMPLEMENTATION CONCERNS, ADVANTAGES AND DISADVANTAGES

- With all *in situ* treatment, it is critical to understand the hydrogeology of the site and determine if the reagents can be deployed to all areas of interest. If the reagent cannot be effectively deployed, alternative treatment may need to be considered.

- Testing often needs to be conducted prior to treatment to understand the correct reagent or substrate. A combined understanding of site hydrogeology and general idea of rates of chemical reaction and mobility of additives are needed to design and implement the system. If these are not considered, unexpected issues such as biofouling, plugging of aquifer (e.g., with ferrous injection) and undesired mobilization of other metals, organic compounds and/or ammonia may result.

- Enough data need to be collected to determine if the products from treatment may interact with soil down-gradient of the treatment to cause problems.

- Changing redox conditions can mobilize metals such as arsenic, iron, and manganese. The treatment needs to account for these.

- Chemical or biological treatments may have byproducts, e.g., SO_4^{2-} or SO_2, that may have regulatory or safety standards that need to be accounted for in project work plans.

- Injection of soluble chemicals or biological treatment has the advantage of not having to excavate contaminated material (reducing health and safety issues) and is generally less expensive than PRBs.

- *In situ* treatments are most always less expensive than conventional P&T. With in-situ treatment, large quantities of water do not have to be treated and disposed, as with the P&T processes.

- An advantage of using injection galleries, e.g., CaS_x at Ecodyne, is that Cr(VI) associated with soils in the unsaturated zone can be treated as well as in the saturated zone.

- As demonstrated at the Selma site, depths greater than 120 ft deep can be treated.

- These electrochemical reductive treatments of Cr(VI) do not remove chromium from the site, but convert it to a non-mobile, low toxicity component of the subsurface soil media.

- The price to remediate low permeability sites will be higher than more permeable sites.

- Direct-push technologies are often more applicable to treatment of smaller areas with higher concentrations of contaminants. Recirculation systems are applicable to many situations. The choice of application is site specific.

- Recirculation systems can also be used to control hydraulic flow of treated and surrounding untreated water.

- The project team must work closely with the regulators to ensure all project components are approved and can be implemented, such as reinjection of treated water in a recirculation system.

10.5 CONCLUSIONS

Chromium contamination is an issue at many sites. Historically these contaminated sites have been remediated by either excavating the contaminated soil or the use of P&T systems. Cr(VI) contamination typically exists as an oxyanion Cr(VI) or biCr(VI) in groundwater and is very mobile. The more reduced form of chromium, Cr(III), is a required trace nutrient for humans and forms hydroxides that have low toxicity and very low mobility.

The drinking water criteria for groundwater treatment for Cr(VI) is low and will probably be lower in the future. There is a number of *in situ* treatment options available including:

- Biological

- Chemical

- ZVI

- Natural Attenuation.

The first three options may be applied using gravity feed via wells or infiltration galleries, direct push, recirculation, and for ZVI – emplacement. *In situ* treatment with recirculation of groundwater may shorten treatment duration compared to other application methods at many sites. Each site needs to consider life-cycle costs to determine which treatment will be most cost-effective.

10.5 REFERENCES

Ahmad, H., 2004. Evaluation and enhancement of electro-kinetic technology for Remediation of chromium copper arsenic from clayey soil, Chapter II – Literature Review, The Florida State University College of Engineering.

Gemoets, J., Gielen, C., Hermands, N., Vermoortel, Y., and Carpels, M., 2003. Evaluation of the potential for natural attenuation and in situ bioprecipitation of chromium in groundwater, Paper L-07, in Magar, V.S., and M.E. Kelley, M.E., eds., *In Situ* and On Site Bioremediation-2003, Proceedings of the Seventh International *In Situ* and On-Ste Bioremediation Symposium (Orlando, FL: June 2003), ISBN 1-57477-139-6, Published by Battelle Press, Columbus, OH.

Hem, J. D., 1985. Study and interpretation of the chemical characteristics of natural water, Third Edition, U.S. Department of the Interior, United States Geological Survey Water-Supply Paper 2254.

Henny, C., Weathers, L.J., Katz, L.E., and MacRae, J.D., 2001. Abiotic and biotic Cr(VI) reduction in a laboratory-scale permeable reaction barrier, Leeson, A., Peyton, B.M., Means J.L., and Magar, V.S., eds., *In Situ* and On Site Bioremediation-2001, Proceedings of the International *In Situ* and On Site Bioremediation Symposium (San Diego CA: June 4-7, 2001), ISBN 1-57477-119-6, Published by Battelle Press, Columbus, OH.

Lovley, D.R., 1993. Dissimilatory metal reduction, Annual Review Microbiology. 47:263-290.

McLean, J., and Beveridge, T.J., 2001. Chromate reduction by a pseudomonad isolated from a site contaminated with chromated copper arsenate, Applied and Environmental Microbiology 67:3:1076-1084.

Palmer, C.D., and Wittbrodt, P.R., 1991. Processes affecting the remediation of chromium-contaminated sites, Environmental Health Perspectives 92:25-40.

Perlmutter, M., Britto, R., Cowan, J.D., and Jacobs, A.K., 2001. *In Situ* biotreatment of perchlorate and chromium in groundwater, Leeson, A., Peyton, B.M., Means J.L., and Magar, V.S., eds., *In Situ* and On Site Bioremediation-2001, Proceedings of the International *In Situ* and On Site Bioremediation Symposium (San Diego CA: June 4-7, 2001), ISBN 1-57477-119-6, Published by Battelle Press, Columbus, OH.

Phifer, M.A., Turick, C.E., Millings, M.R., Sappington, F.C., McKinsey, P.C., Bayer, C.L., and Jeffrey A. Ross, J.A., 2003. Sulfate reduction remediation of a metals plume through organic injection groundwater, Paper L-04, in Magar, V.S., and M.E. Kelley, M.E., eds., *In Situ* and On Site Bioremediation-2003, Proceedings of the Seventh International *In Situ* and On-Ste Bioremediation Symposium (Orlando, FL: June 2003), ISBN 1-57477-139-6, Published by Battelle Press, Columbus, OH.

USEPA, 1994. EPA ground water issue, natural attenuation of hexavalent chromium in groundwater and soils, Palmer, C.D., and Puls, R.W., EPA/5405/5-94/505, October.

USEPA, 2000. *In Situ* treatment of soil and groundwater contaminated with chromium, Technical Resource Guide, EPA/625/R-00/005, October.

APPENDIX A

Workshop Agenda

This page intentionally left blank

AGENDA

Technologies Workshop for Treatment of Chromium in Groundwater
Department of Energy Hanford Site

Consolidated Information Center (CIC Building)
Washington State University Tri-Cities
University Way
Richland WA
April 8-10, 2008

Tuesday, April 8, Room 120 and 120A

8:00-8:10	Welcome and Introductions	Briant Charboneau and Chris Sutton
8:10-8:15	Workshop Objectives and Logistics	Chris Sutton and Dawn Kaback
8:15-8:30	Regulatory Perspective	EPA and Ecology
8:30-9:00	Hanford Site Geology and 100 Area Chromium Plumes	Scott Petersen
9:00-9:30	Overview of Chromium Plume Remediation	Ron Jackson
9:30-10:00	100 Area Pump and Treat	Jeff Riddelle
10:00-10:20	100-H Area Electrocoagulation Demo	Scott Petersen
10:20-10:35	Break	
10:35-11:05	100-D Area *In Situ* Redox Barrier	Jim Scezcody and Scott Petersen
11:05-11:30	100-H Area *In Situ* Bioremediation	Mike Truex
11:30-12:00	100-D Area *In Situ* Bioremediation	Mike Truex
12:00-1:00	Lunch	
1:00-1:25	100-K Area Calcium Polysulfide Demo	Scott Petersen
1:25-1:50	100-D Area ZVI Injection	Scott Petersen
1:50-5:00	Site Tour	

Wednesday, April 9, Room 120 and 120-A

8:00-8:45	Environmental Chromium Biogeochemistry	Bruce Wielinga
8:45-9:30	AWWA *Ex-Situ* Bench Scale Alternatives Study	Chad Seidel
9:30-10:15	Reductive *Ex-Situ* Treatment Technologies	Jim Mavis
10:15-10:30	Break	
10:30-11:15	*Ex Situ* Alternatives Based On Discharge Options	Ron Borrego
11:15-12:00	DOE Pantex Cr Treatment	Chris Lyles
12:00-1:00	Lunch	
1:00-1:45	*In Situ* Injection of ZVI	Tom Simpkin
1:45-2:45	*In Situ* Injection of Calcium Polysulfide	Jim Rouse
3:00-3:15	Break	
3:15-4:00	*In Situ* Bioremediation	Jim Harrington

4:00-4:45	ISB and CaSx Case Studies	Ernie Stein

Thursday, April 10, Room TBD

8:00-11:45	Informal Discussions between Fluor, CH2MHill, and Experts

Hanford Speakers
Briant Charboneau - DOE
Scott Petersen – Fluor Hanford
Ron Jackson – Fluor Hanford
Jeffrey Riddelle – Fluor Hanford
Jim Scezcody – PNNL
Mike Truex - PNNL

Expert Speakers
Bruce Wielinga – Geomatrix Consultants
Chad Seidel – Damon S. Williams Associates
Jim Mavis – CH2MHill
Ron Borrego – Geomatrix Consultants
Chris Lyles – Department of Energy Pantex
Tom Simpkin – CH2MHill
Jim Rouse – Montgomery Watson Harza Global, Inc.
Jim Harrington – Alexco Resources
Ernie Stine – Shaw Environmental

APPENDIX B

Workshop Attendees

This page intentionally left blank

Chromium Treatment Technologies Workshop Attendees
April 8-9, 2008

Name	Organization	Phone	Email
Dawn Kaback	Geomatrix	303-534-8722	dkaback@geomatrix.com
John Price	Dept. of Ecology	509-372-7921	jpri461@ecy.wa.gov
Bruce Wielinga	Geomatrix	303-534-8722	bwielinga@geomatrix.com
Ron Borrego	Geomatrix	970-764-4070	rborrego@geomatrix.com
Ted Repasky	CTUIR	541-966-2412	TedRepasky@ctuir.com
Sally Simmons	FGG	509-376-3509	Sally_A_Simmons@rl.gov
Roberta Day	CH2M Hill	509-539-0232	bday@ch2m.com
Jacqui Shea	Dept. of Ecology	509-372-7925	jash461@ecy.wa.gov
Larry Gadbois	EPA	509-376-9884	gadbois.larry@EPA.gov
Edward Mignardot	DOE-Service Center	505-845-6059	emignardot@doeal.gov
Justine Marble	DOE EM-20	301-903-7210	justin.marble@em.doe.gov
Tom Post	DOE	509-301-5686	
Blaine Rowley	DOE EM-20	301-903-2777	blaine.rowley@em.doe.gov
Chad Seidel	DSWA	303-989-2205 Ext 114	cseidel@dswa.net
Jim Hanson	DOE-RL	509-373-9068	James_P_Hanson@rl.gov
John Morse	DOE-RL	509-376-0057	John_G_Morse@rl.gov
David Forehand	FH/GRP/Eng	509-376-9809	G_D_David_Forehand@rl.gov
Briant Charboneau	DOE-RL	509-373-6137	Briant_L_Charboneau@rl.gov
Jeff Gillow	Arcadis	303-471-3446	Jeff.Gillow@arcadis.us.com
Tom Giordano	CH2M Hill	720-286-2745	tgiardan@ch2m.com
Jim V. Rouse	MWH	303-526-5493	jim.rouse@mwhglobal.com
Danny Katzman	LANL	505-667-6333	katzman@lanl.gov
John Sands	DOE-RL	509-372-2282	john_p_sands@rl.gov
Jon Blount	CH2M Hill	774-238-6331	JBlount@ch2m.com
Jim Mavis	CH2M Hill	425-453-5000	jmavis@ch2m.com
Tom Simpkin	CH2M Hill	720-286-5394	tsimpkin@ch2m.com
Bob Popielarczyk	CH2M Hill	509-373-2166	R_S_Bob_popielarczyk@rl.gov
Jim Harrington	Alexco Resource	303-808-9101	jimharrington@alexcoresource.com
Ron Jackson	FH	509-373-3599	Ronald_L_Jackson@rl.gov
Chris Sutton	FH	509-373-3812	Chris_Sutton@rl.gov
Jeff Riddelle	FH	509-372-1684	Jeff_G_Riddelle@rl.gov
Dan Tyler	Freestone	509-943-5222	dantyler@gofreestone.com
Jamie Zeisloft	DOE-RL	509-372-0188	Jamie_zeisloft@rl.gov
Misty Reed	DOE-SRS	803-952-8583	misty.reed@srs.gov
W. Riggbee	YN (Yakama Nation)	509-985-6756	
Alisa Huckaby	Dept. of Ecology	509-372-7909	ahuc461@ecy.wa.gov
Leah Slech	YN/ER/WM	509-985-8001	leah@yakama.com
Dana Miller	YN/ER/WM	509-452-2502	dana@yakama.com
Al Ramos	YN/ER/WM	509-452-2502	aramos@yakama.com
John Cox	CTUIR	541-966-2801	johncox@ctuir.com
Julie Robertson	FH/SGRP	509-376-8162	Julie_R_Robertson@rl.gov
Ernie Stine	Shaw	865-494-7347	ernie.stine@shawgrp.com
*Chris Lyles	DOE Pantex	806-477-7132	clyles@pantex.doe.gov

This page intentionally left blank

DISTRIBUTION

Onsite

10	U.S. Department of Energy Richland Operations Office	
	DOE Public Reading Room	H2-53
	B. L. Charboneau	A6-33
	T. W. Fletcher	A5-11
	J. P. Hanson (5)	A5-11
	J. G. Morse	A6-38
	K. M. Thompson	A6-38
11	Fluor Hanford, Inc.	
	T. G. Brown (3)	E6-44
	R. L. Jackson	E6-35
	D. S. Miller	E6-44
	S. W. Petersen	E6-44
	J. G. Riddelle	E6-35
	A. F. Shattuck	E6-44
	D. J. Shrimpton	E6-44
	S. Sutton	E6-44
	J. A. Winterhalder	E6-35
1	Lockheed Martin Services, Inc.	
	Document Processing Center	H6-08
1	Pacific Northwest National Laboratory	
	Hanford Technical Library	P8-55
2	CH2M Hill	
	R. E. Day	E6-44
	J. Blount	E6-44

This page intentionally left blank