U.S. DEPARTMENT OF ENERGY HANFORD SITE

EVALUATION OF AMENDMENTS FOR MENDING THE ISRM BARRIER

TECHNICAL ASSISTANCE PROJECT #33

FINAL TECHNICAL SOLUTIONS REPORT

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EXECUTIVE SUMMARY

Background

In May of 2004, the U.S. Department of Energy (DOE) Richland and Fluor Hanford requested technical assistance from DOE Headquarters EM-23 to provide a team of technical experts to evaluate likely chemical/biological amendments for mending the In Situ Redox Manipulation (ISRM) Barrier in the 100-D Area of the Hanford Site. This request was a follow-on to an earlier request for assistance regarding the cause of chromium (Cr) breakthrough and recommendations for mending the barrier (March 2004 workshop). This report provides written documentation of the team's findings and recommendations.

In 1995, a plume of dissolved hexavalent chromium [Cr(VI)] was discovered along the Columbia River shoreline and in the 100-D Area. Between 1999 and 2003, a reactive barrier using the ISRM technology, was installed a distance of 680 meters along the river to reduce the Cr(VI) in the groundwater. The ISRM technology creates a treatment zone within the aquifer by injection of sodium dithionite, a strong reducing agent that scavenges dissolved oxygen (DO) from the aquifer and reduces ferric iron [Fe(III)], related metals, and oxy-ions. Bench-scale and field-scale treatability tests were conducted to demonstrate proof-of principle and to estimate barrier longevity, calculated to be in excess of twenty years. However, several years after initial and secondary treatment, groundwater in approximately 17 wells has been found to contain elevated Cr concentrations.

The March 2004 technical assistance team (TAT) identified potential causes of Cr breakthrough as likely related to physical and chemical heterogeneity within the aquifer (including loss of reductive capacity within preferential flow paths) and the presence of other oxidants (DO and nitrate) significantly affecting the reductive capacity of the treated aquifer. These aquifer characteristics may limit the ability of alternative amendments to extend the reducing capacity of the barrier. A 2001 Bechtel Hanford report and evaluation of the ISRM performance data and barrier longevity assessment corroborate the observations and findings of the March 2004 TAT. The March 2004 TAT recommended the collection of new aquifer characterization data in combination with the interpretation of existing data to develop a conceptual model of aquifer heterogeneity to enable design of the most appropriate barrier mending system.

The current TAT was convened to examine the most promising amendment that could be applied to mend the ISRM barrier. The Technical Assistance Team (TAT) performed the following activities:

1) Evaluate the most appropriate single or combination of chemical/biological amendments suitable for increasing the reductive capacity of the ISRM barrier;
2) Evaluate the most practicable means of introducing chemical/biological amendments in the target zones along the current ISRM barrier;

3) Provide recommendations for laboratory treatability-testing protocol development to evaluate the type and delivery mechanisms of amendments in the current ISRM barrier location.

Sections of this report present analyses and recommendations of potential amendments and delivery options to improve performance of the ISRM barrier. The report covers the spectrum of passive barrier mending to chemical and biological amendments that have been shown to perform more efficiently in more active remedial design approaches. Because DOE/RL is considering significant aquifer characterization studies as additional time and cost investment to mending the barrier, the TAT strongly recommends that DOE/RL conduct cost-benefit analyses of alternative designs to mend the barrier. In this way, the value and extent of characterization studies, compared to passive amendment delivery, compared to engineering redesign, can be quantitatively estimated for decision-making purposes.

Chemical/Biological Amendments Considered

The TAT considered several potential amendments for mending the barrier: dithionite, calcium polysulfide, micron-scale iron, nano-scale iron, dissolved iron, and biostimulants. The amendments were evaluated using the following criteria: effectiveness, implementability, maintenance (longevity), safety, regulatory acceptance, and cost.

The TAT recommended that the following amendments be further considered: 1) calcium polysulfide with organic substrate injected using a process and system design similar to previous reductant injections, 2) micro- and nano-scale iron injected within targeted preferential pathways in the aquifer. Given the current limited knowledge of the physical and chemical character of the aquifer, the TAT believes that dithionite should not be considered for mending, as its long-term performance may be limited by the availability of reduced iron in the preferential pathways within the aquifer. The TAT also recommended no further consideration of liquid iron, as past performance at some field sites has shown problems with cementation of the aquifer, thus reducing permeability. Because the most cost-effective approach to mending the passive barrier using ZVI may require targeting of preferential flow paths for injection, a conceptual model based upon detailed characterization of aquifer heterogeneity to target the location and extent of preferential flow paths will be required. Injection of calcium polysulfide, coupled with an inexpensive organic substrate, is expected to promote enhanced reductive capacity with longevity equal to, or perhaps greater than, the sodium dithionite. These two amendment approaches must be further evaluated with laboratory and field testing before a preferred alternative can be selected.

Issues related to performance and delivery of amendments must be tested prior to selection of a specific amendment. For example, possible formation of ammonia as a product of nitrate reduction with ZVI amendment must be examined, because of potential environmental effects. Results from current or planned demonstrations of calcium polysulfide plus organic substrate in the 100-K Area, and organic-substrate amendment in the 100-H Area should be used to support the amendment-selection process.

Delivery of Amendments into the Aquifer

The TAT evaluated the delivery of the various amendments into the aquifer, as a component of the overall project cost when combined with the longevity of the reduction. Calcium polysulfide and biostimulants can both be delivered to the aquifer in liquid form, similar to dithionite. No specific delivery issues are anticipated, although the physical heterogeneity of the aquifer will control movement of the fluids through the subsurface. These amendments can be utilized in the current barrier injection wells, as creation of a continuous barrier was demonstrated with the dithionite. On the other hand, delivery of ZVI amendments is less proven and may be problematical in terms of radius of influence. Testing needs to be done to evaluate delivery of ZVI amendment.

Longevity of the potential amendments must be evaluated in terms of amendment cost. For example, although ZVI material costs are significantly higher than the biostimulants, greater longevity of ZVI would require much less injection compared to biostimulants, which would require almost continuous injection. This may result in similar life-cycle cost for both the amendments.

The ISRM barrier, as it currently stands, can be used as a containment option with periodic injections of reductant (i.e., operating the barrier in the passive mode) so long as proper aquifer characterization is done. However, this option could prove to be expensive in the long run (detailed cost-benefit analysis should be performed following treatability testing) and it is the TAT's belief that a more active remediation will be required for the final remedy solution. During the evaluation of methods for introducing amendments to the aquifer, the TAT identified three approaches for active remediation of both the source zone and the dissolved plume, which build upon the current infrastructure of the passive barrier:

1. Source Treatment with the Passive Barrier
2. Source Treatment with Hydraulic Control and Active Treatment in the Barrier;
3. Source Treatment with Hydraulic Control and Active Treatment in the Dissolved Plume and the Barrier.

Option 1 proposes the use of calcium polysulfide plus organic substrate as the source treatment in combination with ZVI amendment for mending the passive barrier. Options 2 and 3 propose the use of calcium polysulfide plus organic substrate in active treatment modes. Addition of ZVI to enhance the performance of the calcium polysulfide plus organic substrate could be considered based upon the results of the treatability testing.

Laboratory-Treatability and Field-Testing Recommendations

Both laboratory (batch and column tests) and field-testing should be designed to evaluate effectiveness, longevity, cost, and implementability for each amendment. Specific treatment parameters to be determined include: rate of reduction, reaction products, speciation and stability of reduced Cr, ability to treat source zone, amendment reduction capacity, longevity, and deactivation rate, relationship between reduction capacity and hydraulic conductivity of the aquifer, methods to deliver the amendment, and reductant mobility and fate. Field testing should include: 1) hydraulic testing to determine physical heterogeneity and changes in hydraulic conductivity due to addition of amendments, 2) amendment injection to determine rate of transport and changes in hydraulic conductivity, 3) push-pull testing to determine in situ rates of reduction and capacity, and 4) monitoring for performance and potential loss of reductant. This type of testing of potential amendments is critical to compare performance as a basis for amendment selection and ultimately for design of the system.

1.0 INTRODUCTION

1.1 Technical Assistance Request

In May of 2004, the U.S. Department of Energy (DOE) Richland (RL) and Fluor Hanford requested technical assistance from the DOE Headquarters EM-23, Core Technical Group to provide a team of technical experts to develop recommendations on suitable chemical/biological amendments for mending the In Situ Redox Manipulation (ISRM) Barrier in the 100-D Area of the Hanford Site in Washington State. Appendix A contains the original technical assistance request.

To accommodate this request, the Core Technical Group convened a group of technical experts to participate in a 3-day workshop with the objectives of (1) identifying the most appropriate single, or combination, of chemical/biological amendments suitable for increasing the reductive capacity of the ISRM barrier, and (2) providing recommendations on the most practical means to deliver amendments to the target area. Technical experts from industry, universities, and national laboratories with expertise in aqueous geochemistry, hydrogeology, microbiology, permeable reactive barriers (PRBs), and amendment technologies were identified as technical assistance team (TAT) participants. Appendix B provides contact information for the TAT members and others who attended the workshop in Richland, WA, from July 26 through 29, 2004. Appendix C provides the Workshop Agenda.

1.2 Amendments Team

The TAT was composed of the following individuals:

- Beth Moore, US DOE HQ; Hydrogeologist and Review Project Manager
- Rajat Ghosh, Ph.D., The RETEC Group, Inc., Environmental Engineer and Review Team Leader
- Carl Palmer, Ph.D., Idaho National Engineering Laboratory, Hydrogeologist/Geochemist
- Dawn Kaback, Ph.D., Concurrent Technologies Corporation, Geochemist
- Bruce Wielinga, Ph.D., MFG Inc., Biogeochemist
- Jim Rouse, Montomery Watson Harza, Hydrogeologist
- Greg Lowry, Ph.D., Carnegie Mellon University, Environmental Engineer
- Wei-Xian Zhang, Ph.D., Lehigh University, Environmental Engineer
- Kirk Cantrell, Ph.D., Pacific Northwest National Laboratory (PNNL), Geochemist

1.3 Site History and Regulatory Framework

From 1944 through 1967, large volumes of Columbia River water were used to cool the Hanford D and DR Reactors. To protect the reactor equipment, sodium dichromate-dihydrate was added to the cooling water to inhibit corrosion. The geometry of the roughly- delineated chromium (Cr) plume, discovered in 1995 along the Columbia River and in the 100-D Area groundwater, suggests that the release(s) occurred near the facility where water was treated, before it was used in the reactors. In 1997, a treatability test was implemented in one well in the 100-H Area to test ISRM as an in situ treatment solution. In 1998, a second demonstration of the ISRM concept using five wells in the downgradient portion of the plume in the 100-D Area was conducted. In 1995 (DOE, 1995), the interim remedial measure for the 100-HR-3 operable unit was identified as groundwater pump and treat, while allowing for the possibility of implementing alternative technologies such as ISRM. In 1999, the Interim Record of Decision (ROD) for this operable unit, 100-HR-3, was modified to select ISRM in a barrier, located in the downgradient portion of the plume, upgradient of the Columbia River, as the alternative for the 100-D/DR plume. The following remedial action objectives (RAOs) were identified in the Interim ROD and the ROD Amendment (EPA et al., 1996; EPA et al., 1999):

- Protect aquatic receptors in the river bottom substrate from contaminants in groundwater entering the Columbia River;
- Protect human health by preventing exposure to contaminants in the groundwater;
- Provide information that will lead to a final remedy.

The key design elements of the ISRM barrier identified in the ROD Amendment (EPA et al., 1999) and RDA/RAWP (DOE-RL, 2000) are as follows:

- The treatment zone shall treat the Cr plume to 20 parts per billion (ppb) or less at the downgradient compliance wells to achieve 10 ug/L at the river;
- If barrier breakthrough is identified, the Washington State Department of Ecology and EPA will determine alternative action to be taken.

In three phases between 1999 and 2003, the ISRM barrier was installed to its current length of 680 meters to intercept and reduce Cr VI) in the groundwater to less mobile trivalent Cr [Cr(III)] before it reaches the Columbia River. It was emplaced by drilling ~70 boreholes into the aquifer, installing wells for injection of sodium dithionite to induce reducing conditions in the aquifer. Sodium dithionite reduces Cr(VI) through an indirect reaction that requires the presence of reactive iron in the aquifer to be released as ferrous iron, which in turn, reduces the Cr(VI). The wells were installed in a staggered line with a distance of approximately 35 feet between wells. ISRM relies on naturally occurring iron to reduce Cr(VI). Field and laboratory tests performed before the barrier was installed indicated that it should maintain its reductive capacity for approximately 20 years. However, approximately 17 wells within the PRB have shown signs of failure after only a few years of operation.

This situation impacts final closure of the 100-HR-3 Operable Unit, because ISRM must be shown to be robust and reliable to be considered a final solution. Recent planning to extend the barrier, requested by the Washington State Department of Ecology, has been suspended because of strong indications that barrier breakdown is accelerating. In lieu of this extension a temporary pump-and-treat system has been installed and is currently operational at 50 gallons per minute (gpm).

Because of the premature breakthrough of Cr in the vicinity of the barrier, a TAT was assembled in March of 2004 to investigate the probable causes of the barrier breakthrough and recommend solutions to the problem of premature breakdown of reduction capacity in the barrier. The March 2004 TAT recommendations included further characterization of the aquifer in the vicinity of the barrier, specifically identifying a number of tools and approaches that should be considered.

As a result of the March 2004 TAT recommendations, the current TAT was convened to further examine alternative amendments for mending the barrier. This report documents the recommendations of the July 2004 TAT.

1.4 Technical Assistance Objectives

Workshop objectives provided to the TAT by DOE Richland and Fluor Hanford include:

1) Evaluate the most appropriate single or combination of chemical/biological amendments suitable for increasing the reductive capacity of the ISRM barrier.
2) Evaluate the most practicable means of introducing chemical/biological amendments in the target zones along the current ISRM barrier.
3) Provide recommendations for laboratory treatability testing protocol development to evaluate the type and delivery mechanisms of amendments in the current ISRM barrier location.

The TAT provided an out-briefing of their preliminary findings and recommendations to close out the workshop on July 29, 2004. This report documents the recommendations of the TAT, emphasizing evaluation of the optimum mix of amendment(s) to meet DOE-RL's requested objectives and delivery issues pertinent to ROD requirement for establishing a remedy by 2012.

2.0 RECOMMENDATIONS ON MENDING THE BARRIER (MARCH 2004 TAT)

The March 2004 TAT identified two probable causes for premature breakdown in reductive capacity of the aquifer in the 100-D Area: 1) physical and mineralogic heterogeneity within the aquifer, and 2) the presence of other oxidants, such as nitrate (NO_3^-), which were not recognized in the earliest predictions of barrier longevity. In 2001, a Bechtel Hanford report titled "Summary of Evaluation of the ISRM Data and Current Status of the Barrier Longevity" reported the standard deviation on the number of pore volumes required to deplete the reductive capacity of field-treated cores was relatively large compared to the mean (174 ± 115). The range of the standard deviation when compared to the mean suggests insufficient reductive capacity of portions of the dithionite-treated aquifer zones. Additionally, heterogeneity within the aquifer is a significant issue in terms of predictable barrier performance. This report also stated that the original barrier longevity determination was based upon average conditions, which would not be representative in such a heterogeneous aquifer. Barrier integrity based upon a 20 ug/l goal was predicted to fail when as little as 1.5% of the flow breaks through (Farrell et al., 2001).

The TAT recommended that detailed physical and chemical characterization of the barrier be performed to delineate aquifer heterogeneity, prior to mending of the barrier. The TAT also identified alternative methods to induce reducing conditions for mending of the barrier. Because the sodium-dithionite reduction pathway requires the presence of reactive iron (Fe) in the aquifer and because there may not be sufficient reactive iron in some parts of the aquifer (e.g., high-permeability preferential pathways may be flushed of reactive iron), the TAT identified reductants that react directly with Cr(VI) (thus not requiring the presence of reactive Fe), including calcium polysulfide (CaS_5), zero-valent iron (ZVI), aqueous ferrous iron (Fe[II]), and biostimulants, to be further considered. However, these alternative reductants may require frequent delivery due to the excessive flow within the preferential pathways.

This TAT strongly endorses the recommendations provided in the May 2004 Technical Solutions Report and urges that a site conceptual model, developed using existing and new characterization data, be in place prior to the implementation of any recommendations pertaining to the mending of the barrier. As part of the site conceptual model, the TAT recommends that existing and new characterization data be utilized to map the location and extent of preferential pathways. To the extent possible, the site conceptual model should tie together source location, plume delineation, and preferential pathway information. With better understanding of the subsurface flow and transport mechanisms controlling plume flow to the barrier, and with results of laboratory and field testing of amendments, a decision regarding design of a system that either targets injection of selected amendments into high-conductivity zones or one that is applied throughout the aquifer can be made.

Sections 3.0 and 4.0 of this report present analyses and recommendations of potential amendments and delivery options to improve performance of the ISRM barrier. The report covers the spectrum of passive barrier mending to chemical and biological amendments that have been shown to perform more efficiently in more active remedial design approaches. Because DOE/RL is considering significant aquifer characterization studies as additional time and cost investment to mending the barrier, the TAT strongly recommends that DOE/RL conduct cost-benefit analyses of alternative designs to mend the barrier. In this way, the value and extent of characterization studies, compared to passive amendment delivery, compared to engineering redesign, can be quantitatively estimated for decision-making purposes.

3.0 POTENTIAL AMENDMENTS

3.1 Amendments Considered

The TAT evaluated the six amendments identified by the March 2004 TAT for mending the barrier:

1) Dithionite

2) Calcium polysulfide (CaS_5)
3) Micro-scale iron
4) Nano-scale iron
5) Dissolved iron (e.g. ferrous sulfate)
6) Biostimulants.

3.1.1 Dithionite

The initial barrier design assumed a treatment life of 20 years using sodium dithionite to reduce Cr(VI) in the groundwater Dithionite injections along the barrier created a continuous barrier for 3-4 years. Recent monitoring data indicate premature breakthrough of Cr along the barrier in a number of wells.

The sustainability of reducing conditions using the dithionite lixiviant relies upon the presence of sufficient reactive iron in the subsurface. Therefore, the determination of whether there is sufficient reactive iron (e.g., submeter scale) remaining in the subsurface is prerequisite to evaluating the practicality of dithionite re-injection. The TAT recommends that additional characterization studies be conducted to determine if sufficient reducible iron is present in the highly conductive zones within the aquifer to assess the feasibility of dithionite re-injection.

Limited evidence for insufficient reactive iron in the high-conductivity zones includes: 1) a direct correlation between relative permeability in the high-permeability zones and the observed Cr breakthrough (DOE, 2004), and 2) loss of reductive capacity is observed in many of the sediment cores at depths corresponding to the depth interval of the highly conductive zones (see Appendix GG in DOE, 2003).

Given the available data, it is the opinion of this TAT, that dithionite amendment alone is unlikely to provide a cost-effective solution for treatment of the Cr in the groundwater using the passive barrier. As such, dithionite-mediated treatment of Cr(VI) is not evaluated further in this report. The recommended aquifer characterization data should provide further information about the viability of dithionite reinjection as a solution.

3.1.2 Calcium Polysulfide

Calcium polysulfide (CaS_5), which is water soluble, has been demonstrated as a successful metal-fixating agent for many heavy metals (e.g., arsenic, lead, copper, cadmium), precipitating metals as less soluble and non-toxic sulfides. When mixed with water, polysulfide dissociates to form bisulfide (HS^-) and aqueous hydrogen sulfide ($H_2S_{(aq)}$) with the relative percentage a function of the solution pH. The sulfide can react directly with the Cr(VI) to form Cr(III). Alternatively, the sulfide can reduce Fe(III) present in the aquifer to Fe(II). Fe(II) then reduces Cr(VI) entering the reduced zone. In the pH range of 4-10, Cr(III) will precipitate as $Cr(OH)_3$ and Cr(III) concentrations will be < 1 μM (52 μm/L). If reduction is by Fe(II), Cr(III) will coprecipitate with Fe(III) to form the less soluble $Fe_{0.75}Cr_{0.25}(OH)_3$, and the Cr(III) concentrations will be even lower (Sass and Rai, 1987). All the possible reactions are too numerous to describe in this report; however, a generalized equation describing the overall process is given by equation 1:

$$2CrO_4^{2-} + 3CaS_5 + 10H^+ \rightarrow 2Cr(OH)_3 + 15S + 3Ca^{2+} + 2H_2O \qquad (1)$$

Chromium hydroxide is much less soluble in the neutral pH region between 7 and 9, with solubility increasing both under acidic and alkaline conditions. Reducing conditions created following the addition of CaS_5 enable reduction of other oxidized species such as Fe(III) to Fe(II), which could in turn enhance the reduction of Cr(VI) according to equation 2:

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

As the reaction between CaS_5 and Cr(VI) takes place in groundwater, most of the sulfur precipitates as elemental sulfur, although a minor amount oxidizes to sulfate (SO_4^{-2}). The reduced conditions in the aquifer promote the growth of naturally-occurring sulfate-reducing bacteria (SRB) that reduce the native and additional SO_4^{-2} back to sulfide, thereby achieving further reduction of Cr(VI) and will prevent SO_4^{-2} from exceeding secondary drinking water standards. CaS_5 can also reduce nitrate (NO_3^-) to nitrogen gas (N_2) (Jenneman and Gervertz, 1999).

The carbon source for the SRBs can be natural organic matter in the soil. While many sites contain sufficient total organic carbon (TOC) to support a SRB population, active remediation projects frequently result in the depletion of the native TOC concentrations. Therefore, TOC often needs to be added in the form of molasses, corn syrup, ethanol, lactate, potato waste, or virtually any available waste carbon source.[1]

CaS_5 is sold as a 29 % aqueous solution of CaS_5. Commercial quantities are available in 55-gallon drums, ‘totes,’ or bulk tanker shipments from at least two manufacturers. Also referred to as “lime sulfur solution,” it is a deep orange-red, alkaline solution with a pH between 11.3 and 11.5, and a specific gravity of 1.273. It has received a National Sanitation Foundation approval for use in potable aquifers, and is widely used in agricultural applications to fruit trees and as a soil conditioner.

Numerous applications, specifically for Cr(VI), have been successfully conducted at industrial sites over the last ten years (Blessing and Rouse, 2002).

3.1.3 Solid and Liquid Iron Additives

Injection of both solid, as ZVI, and liquid forms, as ferrous iron, has been investigated for aquifer treatment. Solid ZVI has been developed in micron-scale and nano-scale forms

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[1] Waste byproducts from potato processing are abundantly available in the Tri-Cities area. Laboratory tests evaluating potato processing waste for pit lake remediation indicated that these wastes were an excellent nutrient for microbial respiration and effective at promoting in situ redox manipulation (Castro et al., 1999). A potential drawback of this waste compared to other products (e.g., corn syrup or ethanol) is the presence of solids in process wastes, which could potentially plug wells and/or infiltration galleries.

for injection as a powder. It has triple the reducing power of dithionite, producing three electrons for Cr(VI) reduction as compared to one electron during ferrous iron reduction generated by the addition of dithionite. Solid ZVI releases electrons much more slowly than liquid forms of iron, either injected directly or generated through reaction of dithionite. It is well known that in the presence of ZVI, Cr(VI) undergoes direct, rapid reduction to thermodynamically stable Cr(III), which then precipitates as chromium hydroxide or forms solid solution with iron. The entire reaction is outlined by equation 3:

$$3Fe^0 + CrO_4^{2-} + 8H_2O + 2H^+ = 4Fe_{0.75}Cr_{0.25}(OH)_3 + 3H_2 \qquad (3)$$

To minimize costs of mending the barrier, iron additions could be designed for emplacement only in the high-permeability intervals, or only in those areas where preferential pathways have been identified. Targeting preferential pathways for injection in each well would require more detailed aquifer characterization,increasing costs of characterization but possibly decreasing the cost of treatment.

3.1.3.1 Micron-Scale Zero-Valent Iron Emplaced with Shear-Thinning Polymers

An innovative approach for emplacement of ZVI into an aquifer is injection of suspensions of colloidal-sized (1 μm - 3 μm diameter) iron particles. Because only a few weight-percent iron is emplaced into the aquifer, no significant effect on hydraulic conductivity is expected.

Bench-scale laboratory experiments, conducted by PNNL, focused on use of polymer additives (steric stabilizers and rheological modifiers) to greatly reduce particle-particle interaction and particle settling. Injection of these suspensions into porous media demonstrate no adsorption of the polymer material on the aquifer materials and fairly even distribution of iron throughout the column. This work was conducted using both quartz sand and natural Hanford aquifer materials (Kaplan et al. 1994; Kaplan et al. 1996; Cantrell and Kaplan 1997, Cantrell et al., 1997, and unpublished results discussed in the previous ISRM TAT report provided in DOE (2004)). Because these suspensions have a higher viscosity than water, they tend to flow preferentially to the more permeable zones where treatment is needed.

3.1.3.2 Nano-Scale Zero-Valent Iron

Nano-scale ZVI has been tested as an in situ reductant since the late 1990’s (Elliot and Zhang, 2001; Wang and Zhang, 1997; Lien and Zhang, 1999, 2001; Schrick et. al. 2002, 2004; Zhang, 2003; Ponder et. al., 2000, 2001; Lowry and Johnson, 2004). The ability of nano-scale iron to reduce Cr(VI) has been demonstrated (Ponder, et al., 2000). Nano-scale iron is about 10 to 1,000 times more reactive than conventional iron powders and because of the smaller (~nm) particle size has much greater surface area available for reaction. Nano-scale iron can be suspended in slurry and pumped directly into the target contaminant zones through the injection wells or using a direct-push rig, such as the Enhanced Access Penetration System (EAPS) recently demonstrated at Hanford. The ideal size range of the nano-scale particles for subsurface application is between 100 and

500 nm, which is large enough to obviate attractive forces between the mineral matrix and the iron, while also small enough to minimize gravitational settling (Elliot and Zhang, 2001).

There are currently three methods that produce nano-scale colloids with optimal reactivity and longevity. These are: (1) aqueous synthesis of nano-scale iron with borohydride (Wang and Zhang, 1997), (2) production of nano-scale colloids using a modification of conventional ball-milling techniques (Pekala et al., 1999; Revesz et al., 2000), and (3) gas-phase reduction of iron-oxides using hydrogen gas (Uegami, et al., 2003). Although the borohydride precipitation method is designed to impart longer reactive life than conventional iron filings, or ferragel-supported nano-scale colloids (Ponder et al., 2001), the primary disadvantage of this form is its high cost of production per pound of the material. Recently, Lehigh University developed a new chemical route to manufacture these particles, which may lower the cost per pound from \$250/lb to \$20/lb (http://www.nsf.gov/od/lpa/news/03/pr0394.htm). Particles made from gas-phase reduction of iron oxide are commercially available from Toda, America, Inc. for approximately \$15/kg for a 25 wt % particle slurry. Although the cost is higher than conventional iron filings, the ability to better deliver this material to subsurface targets could drive the economics in favor of the nano-scale colloids.

3.1.3.3 Dissolved Iron

Supplemental Fe[II] could be added to iron-depleted zones, such as preferential pathways, or throughout the aquifer to add reductive mass. An aqueous mending agent has an advantage over a particulate agent in terms of its ability to disperse within the aquifer to greater distances from the injection well. Liquid ferrous iron is inexpensive and will primarily follow the preferential pathways that require the treatment. However, it would need to be fixed within the barrier in some manner to provide continuous treatment capability. The need for multiple injections of liquid $FeSO_4$ might offset the economic benefit.

There are limited field applications of dissolved Fe(II) as a reductant in the subsurface. In principle, Fe(II) should precipitate as ferrous hydroxide according to the following reaction:

$$\begin{aligned} &FeCl_2[\text{dissolved}] + CaCO_3[\text{calcite}] + 2H_2O \\ &\quad = Fe(OH)_2[\text{ferrous hydroxide}] + Ca^{2+} + 2Cl^- + HCO_3^- + H^+ \end{aligned} \tag{4}$$

Recently, the EPA demonstrated Fe(II) precipitation in an aquifer by injecting ferrous sulfate, dissolved in aqueous solution with sodium dithionite added as a redox buffer to help keep iron reduced to Fe(II) (R. Ludwig, include detailed refs need to get this reference). The demonstration was successful at introducing Fe(II) into the formation and Cr concentrations decreased. The pH of the formation at this site was high (about 11), which probably contributed to the formation of ferrous hydroxide. However, even at this high pH, some iron mobility was observed downgradient of the injection (personal communication R. Ludwig to S. Morrison, 2004), and the longevity of liquid iron amendments is questionable, especially in high-conductivity zones. At some sites, introduction of ferrous iron has resulted in cementation and plugging of the aquifer. Some plugging in the high-conductivity zones might be desirable; however, control of this phenomenon would be extremely difficult.

3.1.4 Biostimulants

The direct enzymatic reduction of Cr(VI) by numerous bacteria has been reported (Fredrickson et al., 2000; Lovely, 1993; Lovely and Coates, 1997; Tebo and Obraztsova, 1998), as illustrated by equation 5, in which lactate is shown to be the organic electron donor:

$$C_3H_6O_3 + 4CrO_4^{2-} + 8H^+ \rightarrow 3CO_2 + 4Cr(OH)_3 + H_2 \qquad (5)$$

Microbial reduction of Cr(VI) has been observed under both aerobic and anaerobic conditions. The potential use of biostimulation for reduction and sequestration of Cr has been the subject of numerous investigations and reviews (Losi et al., 1994; Lovely, 1993; Lovely and Coates, 1997). In addition, microbial reduction of Fe(III) and SO_4^{-2} creates potent chemical reductants, Fe(II) and sulfide respectively, that reduce Cr(VI) via the indirect chemical pathway (Fendorf et al., 2002; Wielinga et al., 2001).

3.2 Amendment Selection Criteria

The TAT evaluated potential amendments using the following criteria: effectiveness, implementation, maintenance, safety, regulatory acceptance, cost, and the ability to meet the DOE's accelerated cleanup goal of 2025. A summary of the each evaluation criterion and the metric used for its evaluation is provided in Table 3.1. The recommended parameters to be investigated for each criterion and the rationale are also provided.

3.2.1 Effectiveness

The effectiveness of each amendment is evaluated by several metrics:

- The ability to reduce Cr(VI), in the presence of competing oxidants (NO_3^- and oxygen [O_2]) at the site, at a sufficient rate to meet the barrier design goal of 20 μg/L in the downstream monitoring wells;
- The mass of reductant that must be delivered to the high-conductivity regions to achieve the required Cr(VI) removal rate;
- The potential to produce toxic reaction products (e.g. ammonia [NH_4^+] from NO_3^-) that will harm aquatic receptors in the Columbia River;
- The ability of the proposed amendment to achieve source-zone mass,

Table 3.1. Amendment Selection Criteria Summary

Criterion	Required Parameters	Metric
Effectiveness	Rate of Cr^{6+} reduction	Cr^{6+} reduction rate/kg amendment
	Amendment mass required	
	Production rate of toxic reaction products	Products, production rate and concentration
	Ability to treat source zone	Capable of delivery to the source zone
Implementation	Proven delivery methods	Yes/No (# of sites)
	Able to place in high-conductivity intervals	
	Radius of influence	Delivery distance (m)
	Fate after placement	Potential for migration
	Pore plugging potential	Yes/No (# of sites)
Maintenance (Longevity)	Longevity of reducing conditions	Year
	Frequency of reapplication required	
Safety	Toxicity of amendment and/or byproducts	Excellent, good, poor
	Potential for human exposure	
Regulatory Acceptance	Prior regulatory approval	Yes/No
	Potential for regulatory approval	Excellent, good, poor
Cost	Chemical and delivery costs	High, med, low
	Lifecycle costs	

In calculating the effectiveness of each amendment, the TAT considered the presence of dissolved oxygen (DO) and NO_3^- as competing oxidants, and due to limited characterization data, used bulk aquifer properties based on Williams et al. (2000). The electron equivalents for oxidants present in site groundwater and the average aquifer properties used to estimate the effectiveness of each amendment are provided in Tables 3.2. and 3.3, respectively. Table 3.2 provides electron equivalents for NO_3^- reduction to several potential products (NO_3^-, N_2, and NH_4^+), assuming a continuous influent concentration of 58.8 mg/L of NO_3^-. Complete reduction of a continuous source of 8.4 mg/L of DO and 1.29 mg/L of Cr(VI) is assumed.

3.2.2 Implementability

The ability to effectively deliver the reductants in situ, referred to as the implementability, is an important evaluation criterion. For a reductant to be effective, it must be deliverable to the subsurface and provide a sufficient reducing zone to prevent Cr breakthrough. The following metrics were used to evaluate the implementability of each amendment:

- The ability to adequately deliver the amendment in situ and achieve the required extent and distribution of reductant (i.e., radius of influence and ability to provide a uniform treatment zone);
- The fate of amendments after placement (i.e., their mobility and rate of degradation);
- The potential for pore plugging during and after placement.

Table 3.2. Electron Equivalents to Reduce the Competing Oxidants

Product of NO_3^- Reduction	Electron Equivalents (mmol/L)[1]
No NO_3^- reduction	1.1
Nitrite, NO_2^-	3.0
Nitrogen gas, N_2	5.9
Ammonia, NH_4^+	8.7
No nitrate reduction (Szecsody Assumption)	1.06

[1] Assumes continuous groundwater source of 58.8 mg/L NO_3^-, 8.4 mg/L DO, and 1.29 mg/L Cr(VI). Complete reduction of Cr and O_2 is assumed (Cr(VI) → Cr(III), O_2 → H_2O). For the Szecsody assumption, original calculation with 8.0 mg/L O_2 and 1.0 mg/L Cr(VI) is used.

Table 3.3. Hanford Aquifer Properties

Aquifer Property	Assumed Value[1]
Soil bulk density (g/cm^3)	2.3
Porosity (--)	0.14

[1] Bulk aquifer properties based on Williams et al., 2000

3.2.3 Maintenance

The subsurface longevity of the amendment, referred to as amendment maintenance, dictates the performance of the barrier as well as the time between injections, which is especially critical in a passive system. The proposed amendments were evaluated based on the amount of time they can sustain reducing conditions in the aquifer such that Cr(VI) is immobilized as Cr(III) precipitates, accounting for the known mass flux of DO, NO_3^-, other competing oxidants, and site geochemistry. Table 3.4 presents sensitivity analyses that evaluate the effect of reducible iron, amount of electron acceptors, and groundwater velocity on the longevity of barrier performance when dithionite is used as a chemical reductant. As shown in this figure, the longevity of the barrier could span anywhere from 6 months to 86 years and is extremely sensitive to the groundwater velocity and the amount of reducible iron. Based on estimates of the lifetime of the proposed reductants, the need for reapplication (in a passive system) or the rate of application (in an active remediation system) for each amendment is compared.

3.2.4 Safety

The selection of amendments is also based on the foreseeable health and safety risks to workers applying them. This includes chemical handling, delivery, storage, the demonstrated or suspected toxicity, exposure pathways, and the disposal of unused material.

Table 3.4. Aquifer Longevity Analysis

Sensitivity Analysis	Electron donors (mmol/L)	Pore volumes reduced with various concentrations of electron acceptors		Longevity (YEARS): Time = distance/velocity x p.v.		
				(1 ft/d)	(0.5 ft/d)	(5.0 ft/d)
Best case = maximum reducible iron of 20.3 μmol/g	**334**	297	No Nitrate reduction	41	81	8
		111	Nitrate to Nitrite	15	30	3.0
		57	Nitrate to Nitrogen gas	8	16	1.6
		38	Nitrate to Ammonia	5	11	1.1
		315	No Nitrate reduction (Szecsody)	43	86	9
Heterogeneous case = average reducible iron of 11.2 μmol/g	**184**	164	No Nitrate reduction	22	45	4.5
		61	Nitrate to Nitrite	8	17	1.7
		31	Nitrate to Nitrogen gas	4	9	0.9
		21	Nitrate to Ammonia	3	6	0.6
		174	No Nitrate reduction (Szecsody)	24	48	4.8
Worst case = minimum reducible iron of 2.23 μmol/g	**36.6**	33	No Nitrate reduction	4	9	0.89
		12	Nitrate to Nitrite	1.66	3	0.33
		6	Nitrate to Nitrogen gas	0.85	1.7	0.17
		4	Nitrate to Ammonia	0.58	1.15	0.12
		35	No Nitrate reduction (Szecsody)	5	9	0.95

3.2.5 Regulatory Acceptance

An important consideration for any remedial technology is its acceptance by local, state, and federal regulatory agencies. Technologies that have been proven at other sites and that have already gained regulatory approval will pose lower regulatory hurdles than emerging technologies. The evaluation criterion, therefore, considers the status of the proposed technology and its prior regulatory approval, if it exists.

3.2.6 Cost

Amendment cost is an important evaluation criterion, but is difficult to estimate with certainty in the absence of a field test. Two approaches are used to provide cost estimates for each amendment. First, the cost of alternative amendments can be compared directly with the cost for the dithionite-based ISRM. The chemical cost of the proposed amendment is estimated by assuming some basic geometry and mass of amendment required (Table 3.7). The cost to deliver the amendments (e.g. mobilization, pumping, etc.) is assumed to be similar to those for dithionite delivery in the current ISRM barrier. The estimates assume that the amendment is fully used. Costs are reported as \$/kg Cr(VI) reduced, and as \$/1000 liters of water treated. For amendments that can be applied to the existing barrier and operate passively (micron-scale iron and nano-scale iron), a cost as \$/linear meter/yr lifetime of barrier is provided for comparison to the cost of the current sodium dithionite barrier. The second approach estimates lifecycle costs as the metric to compare active and passive remedial approaches. Lifecycle cost estimates include amendment chemical costs, delivery, pumping, monitoring, as well as operation and maintenance (e.g., periodic well redevelopment).

3.3 Evaluation of Amendments

The amendments listed in Section 3.1, with the exceptions of dithionite and ferrous sulfate (dissolved iron), were evaluated against the six criteria. The TAT excluded dithionite in this evaluation, because it has proven to have significantly shorter longevity as a reductant than predicted for reasons previously discussed. Ferrous sulfate is also excluded in this evaluation, because frequent injections may be required to maintain barrier performance and decreased permeability, due to precipitation of ferric oxyhydroxides, may result. The remainder of this section provides the evaluation of each of the selected amendments against the six criteria.

3.3.1 Calcium Polysulfide with Organic Substrate

CaS_5 accompanied by a low-cost organic substrate has been evaluated as an amendment for mending the Hanford barrier.

3.3.1.1 Effectiveness

CaS_5 has been demonstrated to be highly effective at the rapid reduction of Cr(VI) (Blessing and Rouse, 2002) at industrial sites throughout the United States and Australia. Addition of a carbon substrate enhances the growth of SRB and prevents an increase of SO_4^{-2} concentrations in areas downgradient of the reductant injection (MWH, 2004). It is also capable of reducing NO_3^- to N_2 gas and reducing DO. CaS_5 demands are low, commonly 1 to 3 % of the 29% active ingredient is added to contaminated water to achieve reduction of Cr(VI) concentrations to less than 0.01 mg/l. CaS_5 with carbon-substrate addition has not been shown to create NH_3 from NO_3^-; rather, the NO_3^- is reduced to N_2 gas. It also does not result in the formation of excess SO_4^{-2} ion, but rather, the SO_4^{-2} concentration commonly decreases from ambient conditions as a result of the activity of indigenous SRBs. Because CaS_5 is more stable than dithionite, it has the potential to create a larger reactive zone downstream of the injection wells.

3.3.1.2 Implementation

As a water-soluble reagent, CaS_5 amended with a carbon substrate is readily utilized in in situ applications. The sulfide tends to be flushed downgradient, but the iron reduction is both fixed and mobile. Further, the addition of a carbon source, required to maintain a viable culture, means that the SRB, which are attached organisms, can remain fixed in high-permeability zones. Aquifer plugging has not been observed following multiple injections. Extensive testing of core and groundwater from wells at the Schoolcraft, MI CERCLA site did not show any reduction in permeability (Groundwater Technology, 1995). Much of the sulfur is elemental in form and sorbs onto aquifer solids. The chromium hydroxide is incorporated onto aquifer grains or coatings. When compared to dithionite, CaS_5, in conjunction with some biological substrate, will probably be more effective as an in situ reductant, however, it should also be recognized that this amendment may not provide residual reduction capacity capable of lasting years to decades; thus, the only advantage it may have over the current dithionite-based system may be cost. CaS_5 has proven to be more effective in active remediation with plume control and source treatment.

3.3.1.3 Maintenance

The longevity of CaS_5 and carbon substrate will meet or exceed that of dithionite. The reductant mechanisms are similar, except for the additional benefits provided by SRB. A comparison of CaS_5 with organic substrate to dithionite will require site-specific laboratory- and field-testing and verification to determine costs for long-term maintenance.

3.3.1.4 Safety

CaS_5 is corrosive due to its caustic nature in its concentrated form, but the application of a dilute solution is within normal pH range. Workers are advised to use face shields and gloves in handling the concentrated solution.

Extensive air monitoring at past application sites, including building interiors and around homes, has not detected any generation of hydrogen sulfide, as a reaction between CaS_5 and concentrated acid, in worker breathing space. It is imperative that CaS_5 does not come in contact with concentrated acid during implementation. Nonetheless, CaS_5 has been safely used in the field many times. For example, millions of gallons of CaS_5 are used each year on fruit trees.

3.3.1.5 Regulatory Acceptance

CaS_5 has been accepted by the US Environmental Protection Agency (EPA) and state regulators in California, Massachusetts, Indiana, Colorado, Texas, Maryland, Michigan, and South Australia, for full-scale applications. Regulatory closure has been accomplished in Indiana, Colorado, and South Australia; sites are nearing closure in several other states. The US EPA has declared the Valley Wood Preserving application at Turlock, CA, a success, and is expected to soon consider the site as being remediated.

3.3.1.6 Cost

CaS_5 has a relatively low chemical cost when compared with other amendments, such as dithionite; application of CaS_5 as an “active” remediation strategy will incur costs typical of “active” remedial approaches. More details regarding cost are provided in section 5.4.

3.3.2 Nano-Scale Iron Technologies

The use of iron to rapidly and effectively reduce and immobilize Cr(VI) from groundwater has been well documented in the laboratory and in the field (Alowitz, et al., 2002; Melitas, et al., 2001; Tri-agency PRB Initiative, 2002). Over the last few years, various synthetic methods have been developed to prepare iron nanoparticles, modify the surface properties, and enhance the efficiency of particle delivery and transport. Recent field tests have further demonstrated promise for the use of iron nanoparticles for in situ remediation.

3.3.2.1 Effectiveness

It is well documented that ZVI can reduce certain contaminants, such as some metals and organics, to innocuous compounds via various surface-mediated reactions. The larger the available surface area, the higher the rate of contaminant transformation. For a spherical particle with a diameter of d, specific surface area (SSA) can be calculated using equation 6:

$$SSA = \frac{\text{Surface Area}}{\text{Mass}} = \frac{\pi d^2}{\rho \frac{\pi}{6} d^3} = \frac{6}{\rho d} \tag{6}$$

Where ρ is the density (kg/m^3) of the iron particle. For example, iron filings used in conventional PRB's have diameters on the order of 0.5 mm, and thus, a theoretical specific surface area (SSA) of 1.5x10^{-3} m^2/g. For nano-scale iron particles of 50 nm, the corresponding SSA is ~15 m^2/g. Calculated and measured SSAs for specific types of iron are given in Table 3.5.

Table 3.5. Specific Surface Areas of Spherical Iron Particles

Diameter (d)	SSA (m^2/kg)
1 nm	763,358$^{(1)}$
1 μm	763$^{(1)}$
1 mm	0.763$^{(1)}$
0.4 –2.0 mm$^{(3)}$	1.68$^{(2)}$
1 μm$^{(4)}$	1,000$^{(2)}$
66 nm$^{(5)}$	14,500$^{(2)}$

(1) Calculated using Equation (6) with ρ at 7,860 kg/m^3 for iron.
(2) BET surface area measured with a Micromeritics 20/20 surface area analyzer.
(3) Iron particles from Aldrich (10-40 mesh)
(4) Micro iron particles from BASF
(5) Particles synthesized in laboratory

Table 3.6 presents results from a laboratory study of Cr(VI) reduction by iron nanoparticles. Groundwater and soil samples were collected from an industrial site in New Jersey. The groundwater contained 42.83±0.52 mg Cr(VI)/L, and the soil had 3,280±90 mg Cr(VI)/kg. Cr(VI) in the water and soil samples was quickly reduced and precipitated out of the aqueous solution. One gram of nanoparticles can reduce 84.4-109.3 mg Cr(VI) in the groundwater and 69-73 mg Cr(VI) in soil/groundwater slurries, respectively. This reduction capacity is 50 to 70 times greater than that of micron-scale iron under the same experimental conditions.

Table 3.6. Reductive Capacity of Cr(VI) by Iron

Medium	Nano Fe(0) (mg/g)	Micro Fe(0) (mg/g)
Groundwater	84.4 – 109.3	1.5 – 1.7
Soil in deionized water	64.1 – 76.6	1.2 – 1.3
Soil in groundwater	699.2 – 72.6	1.0 – 1.2

(1) Cao and Zhang, unpublished data
(2) The groundwater contained 42.83±0.52 mg Cr(VI)/L
(3) The soil had 3,280±90 mg Cr(VI)/kg
(4) Micro Fe (0) – 1 µm iron powder produced by BASF
(5) Nano Fe (0) – 50 nm iron nanoparticles prepared at Lehigh University

According to equation 3, the iron-mediated reaction should produce a characteristic increase in solution pH (Figure 3.1). The reactions of iron with water and other oxidants in water (O_2, NO_3^-, SO_4^{-2} etc.) also provide a rapid decrease in solution E_h. The addition of a small amount (e.g., ppm level) of iron particles to water can decrease and maintain the solution E_h to <-400 mV (Figure 3.2). The low redox potential should favor the reduction of Cr(VI) while the slightly higher pH should contribute to the immobilization of the Cr(III) in the soil.

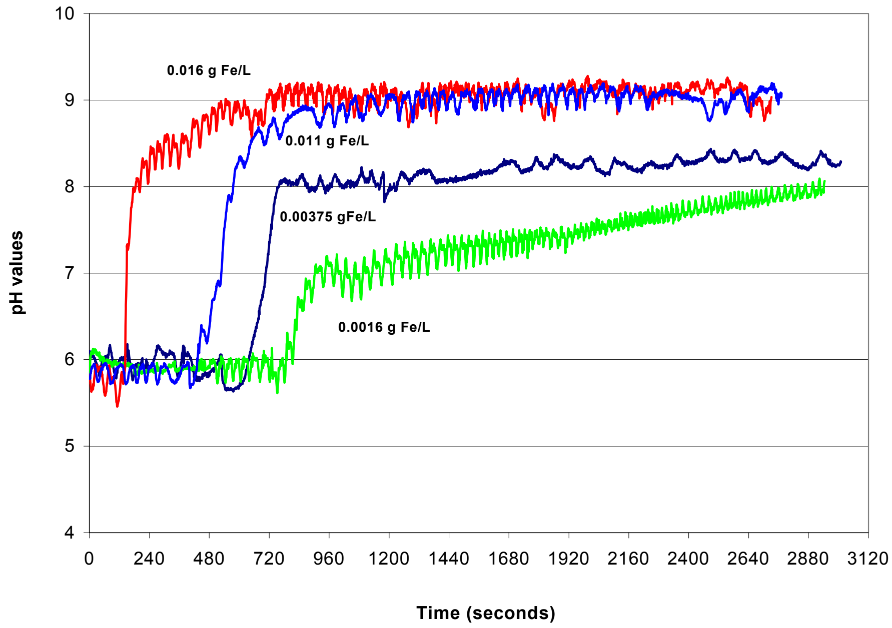

Figure 3.1. Change of Solution pH as a Function of Time and Concentration of Iron Nanoparticles
[The iron nanoparticles (~66 nm) used were prepared at Lehigh University.
(Kravitz & Zhang, unpublished data).]

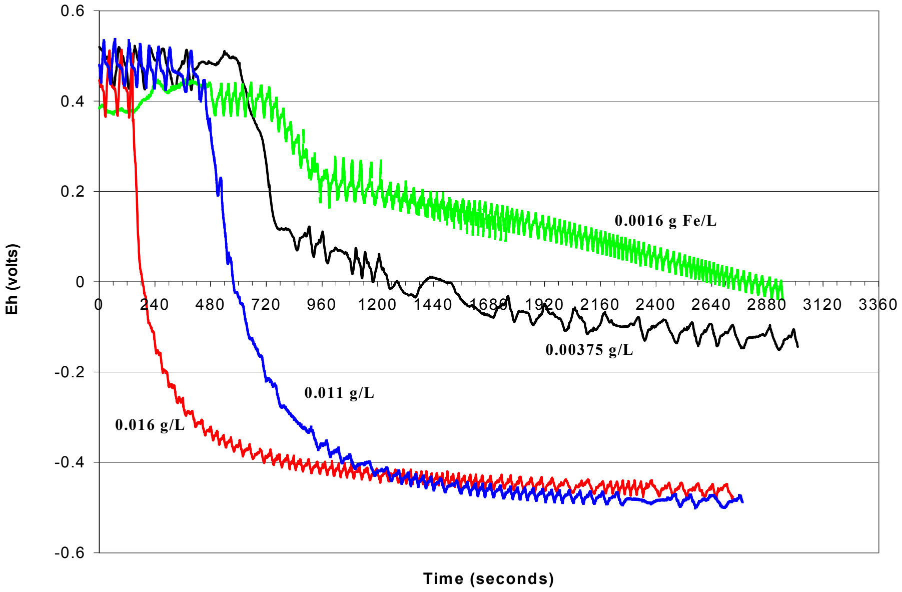

Figure 3.2. Change of Solution Eh as a Function of Time and Concentration of Iron Nanoparticles
[The iron nanoparticles (~66 nm) used were prepared at Lehigh University.
(Kravitz & Zhang, unpublished data).]

3.3.2.2 Implementation

Nano-scale iron can potentially be used to mend and continue operating the barrier passively. The largest uncertainty related to implementation of a nano-scale iron amendment is the ability to deliver the particles to the appropriate locations within the aquifer at a reasonable cost. The ability to deliver iron nanoparticles into heterogeneous aquifers through screened injection wells has been demonstrated (Elliot and Zhang, 2001, Glazier et al., 2003), but the conditions required for controlled and effective delivery have yet to be established. Recently, GeoSyntec, University of Central Florida and NASA Kennedy Space Center conducted a demonstration project to evaluate the technical performance of nano-scale emulsified zero-valent iron (EZVI) technology in the subsurface for treatment of chlorinated DNAPLs at Launch Complex 34 (O'Hara et al., 2004). Nano-scale EZVI was injected in the subsurface in eight wells at a depth of 20-24 ft bgs using pressure pulse technology (PPT). Another demonstration, funded under the auspices of USDOD's Environmental Security Technology Certification Program (ESTCP) is currently underway to evaluate the different delivery approaches to introduce nano-scale iron in the sub-surface (http://www.estcp.org/projects/cleanup/cu-0431.cfm).

An iron particle in water is subject to various forces, e.g., gravitational, electrostatic, and random Brownian motion. For large particles (e.g., > 1 µm), the gravitational force dominates and leads to rapid sedimentation of the particles. For nano-scale iron particles (<100 nm), the random Brownian motion could govern. A relatively stable dispersion of iron particles can form under certain conditions (e.g., in absence of significant attractive forces). Laboratory-and field-testing will be required to determine delivery methods capable of uniform delivery of nano-scale iron into the Hanford Formation, and to determine the mobility of nano-scale iron after placement.

3.3.2.3 Maintenance

Recent field studies indicate that nano-scale iron can provide long-term reducing conditions in the subsurface. The ability of nano-scale iron to maintain reducing conditions in the subsurface also depends on the rate at which nano-scale iron dissociates water to produce H_2 (i.e., the corrosion rate). The rate of H_2 evolution depends on the iron used, and is difficult to predict a priori. The corrosion rate, and the effective dose of nano-scale iron required to maintain a highly reduced redox conditions at the Hanford 100 D area under the influence of both O_2 and NO_3^-, will have to be measured in laboratory and field studies.

3.3.2.4 Safety

Iron is a relatively safe material. It has been widely used successfully in PRBs worldwide.

3.3.2.5 Regulatory Acceptance

ZVI has been used at numerous sites in PRBs and for aboveground treatment. The ability of an iron PRB to effectively treat groundwater contaminated with Cr(VI) was demonstrated at Elizabeth City, NC, and has gained regulatory approval for this purpose. Approval to inject nano-scale iron into aquifers at two field demonstration sites has been granted, primarily to treat chlorinated organics. At Hanford, the high levels of NO_3^- in the groundwater may be a concern to regulators due to the possible transformation of NO_3^- to NH_4^+.

3.3.2.6 Cost

The cost of nano-scale iron is higher than that of conventional iron filings, and is considered to be high relative to other amendments evaluated. The ability to successfully deliver this material into deeper subsurface targets, however, may favor the selection of nano-scale iron in spite of the higher associated cost. Cost considerations are discussed in more detail in Section 5.4.

3.3.3 Micron-Scale Iron

3.3.3.1 Effectiveness

The effectiveness of ZVI toward the reduction of Cr(VI) is well documented in the literature, both in laboratory and field studies (e.g. Powell et al., 1995). However, the reduction of NO_3^- to NH_4^+ by ZVI is a potential adverse reaction. The significance and rates of this reaction under 100-D aquifer conditions should be investigated prior to full-scale use. The use of micron-sized iron for source-zone treatment in the vadose zone is not recommended, because less expensive alternatives are available.

3.3.3.2 Implementation

Injection of micron-scale iron has been demonstrated in Hanford sediments at representative injection rates in column experiments (unpublished results discussed in the previous ISRM TAT report, DOE (2004)). Even distribution at cost-effective concentrations was demonstrated. Once the injection phase was completed, the micron-scale iron was not remobilized by typical Hanford groundwater velocity. It was also demonstrated that the micron-scale iron did not significantly affect porosity or hydraulic conductivity. Most experiments were conducted on one-meter long columns. One three-meter long column experiment was also conducted. Further experiments to determine the maximum viable radius of influence are necessary.

3.3.3.3 Maintenance (Longevity)

The longevity of this approach can be estimated based on the following assumptions. A preferential flowpath that is ten meters long with a diameter of 4.6 m, a porosity of 14%, and a groundwater velocity of 0.33 meters per day is assumed. It is also assumed that the primary oxidants are dissolved O_2 at 8.4 mg/L and NO_3^- at 58.8 mg/L. It is assumed that enough iron is injected to fill 0.5% of the void space in the aquifer. With these assumptions, it is estimated that the “fix” will last approximately 16.5 years.

3.3.3.4 Safety

Because the micron-scale iron is in a powder form, an explosion hazard could result if the powder were to become dispersed in air. The risk of the powder being dispersed in air is very low. The powder is very dense and an active source of high-velocity air would be required to disperse the powder in air. Appropriate precautions such as keeping the material in its transport container until needed would prevent any possible safety issues.

3.3.3.5 Regulatory Acceptance

The use of ZVI for in situ remediation is well established and regulators are generally amenable towards its acceptance as a potential viable groundwater remediation technology.

3.3.3.6 Cost

Micron-scale iron is commercially available at approximately $6.00/lb, and is considered to be of moderate cost relative to the other amendments. More details regarding cost are provided in section 5.4

3.3.4 Biological Substrates in Concert with Chemical Amendments

Recently, it has been shown that microorganisms can change the valence, or oxidation state, of some heavy metals and radionuclides by using then as electron donors or electron acceptors. In some cases, these transformations can result in phases that are more or less soluble and/or have altered toxicological properties. Numerous organic substrates that contain reduced carbon have been used for hydrocarbon and metals remediation. [DAWN – CAN YOU INCLUDE SOMETHING REGARDING THE UWASH STUDY AS INDICATED BY SCOTT PETERSEN IN HIS COMMENTS]

3.3.4.1 Effectiveness

In the 100-D Area groundwater, the most abundant oxidants are DO and NO_3^-. Heterotrophic bacteria are very efficient at removing these constituents from groundwater environments (Hiscock et al., 1991) if a source of organic carbon or other reduced inorganic substrate, such as elemental sulfur, is available. In addition, reduction of Fe(II) and SO_4^{-2} by dissimilatory iron- (DIRB) and SRB can increase reductive capacity of the aquifer via formation of Fe(II) and HS^-, respectively. The reduction of SO_4^{-2} to sulfide also prevents the increase in SO_4^{-2} concentrations in areas downgradient of zones in which reduced sulfur compounds, such as dithionite, have been employed as the primary chemical reductant (Barton and Tomei, 1995; Lovely, 1993). Cr(VI) can be removed via direct enzymatic processes or by reaction with metabolic byproducts, such as, ferrous iron and/or sulfide.

3.3.4.2 Implementation

Typical substrates used for bioremediation are labile organic carbon compounds, such as, carbohydrates, organic acids, and alcohols. Because they can be delivered as dilute, water-soluble reagents, they can be readily used for in situ applications and are amenable for inclusion with other liquid chemical reducing agents. Biostimulants provide a low-cost alternative, but may require frequent or continuous introduction into the subsurface. Indigenous microorganisms (several *Cellulomonas* sp.) in Hanford soil cores were recently determined to be capable of reducing Cr(VI), Fe(III), and uranium [U(VI)] (Sani et al., 2002).

The 2004 demonstration of lactate (HRC™) injection in the 100-H Area at Hanford will provide important information about the use of biostimulants for Cr(VI) reduction.

3.3.4.3 Maintenance

Subsurface microbial populations typically consume labile organic substrates rapidly, and therefore these compounds are expected to have very short half-lives once injected. The reductive capacity of the aquifer can be prolonged under reducing conditions. Under these reducing conditions, the organic substrate enhances the reduction of solid iron oxyhydroxides, present in the aquifer matrix, with the formation of Fe(II) and conversion of SO_4^{-2} to sulfide, which in turn reduces additional Fe(III).

3.3.4.4 Safety

Typical biological substrates are food-grade and/or pharmaceutical-grade compounds that are non-toxic and pose very low health and environmental risks. They are readily broken down in the environment to carbon dioxide and water.

3.3.4.5 Regulatory Acceptance

Bioremediation of organic compound, such as, petroleum hydrocarbons and chlorinated solvents is a technology that has been used extensively for many years. As such, the U.S. EPA and most state regulatory agencies accept injection of organic nutrients to promote enhanced in situ bioremediation.

3.3.4.6 Cost

Costs for biological substrates can vary widely depending on the type of organic compound used. However, they are generally very inexpensive; carbohydrates can often be obtained for <\$0.50 per pound and organic acids for \$2 to \$4 per lb. In addition, industrial waste products that are high in biological oxygen demand (BOD) rather than commercially available products, such as molasses, could contribute to the cost-effectiveness of this remedial approach.

3.4 Amendment Evaluation Summary

Each amendment evaluated has advantages and limitations regarding its ability to effectively maintain reductive zones in the subsurface in the presence of competing oxidants like, O_2 and NO_3^-. Table 3-7 presents the evaluation of the selected amendments against the six criteria. As shown in Table 3-7, CaS_5 in conjunction with organic substrate or ZVI powders (nano/micron) could be deemed as appropriate alternative amendments for the ISRM barrier. However, depending on the type of application, one amendment could be superior over the other.

Although CaS_5 has been shown to have the reducing capability and is easy to deliver, it is still a liquid reagent that could get dispersed and lose its reducing power over long time periods in an oxic aquifer. Nano-scale iron and micron-scale iron, on the other hand, could potentially maintain aquifer reducing capacity over longer periods of time, although, delivery in the target zone and cost of emplacement and chemicals could be a deciding factor for implementation. In either case, detailed hydrogeological characterization of the current barrier and bench-scale treatability tests must be performed to calculate proper dose, longevity, and implementability of such amendments under Hanford site-specific conditions.

Table 3.7. Amendments Prioritization

Amendment	**Evaluation Criteria**					
	Effectiveness	**Implementability**	**Safety**	**Regulatory**	**Longevity**	**Chemical Cost**
Calcium Polysulfide and Organic Substrate	EXCELLENT: Proven in field tests to quickly reduce aquifer; presence of carbon substrate provides additional capacity	EXCELLENT: Proven at multiple field sites for source-zone treatment; liquid injection similar to dithionite	GOOD: Stock solution is corrosive; requires proper handling during mixing	EXCELLENT: Accepted by multiple state and EPA regulators	GOOD: Comparable to or better than dithionite; multiple injections could be necessary to maintain reducing oxidations	[1]LOW: \$800-1200/kg Cr(VI) reduced, \$1-2/1000L water treated
Micron-scale Iron	EXCELLENT: ZVI is proven to reduce Cr(VI) in the laboratory and field PRBs	GOOD: Concern regarding delivery; laboratory injection with shear thinning fluids demonstrated	EXCELLENT: Potential explosive and inhalation hazard for powdered form	EXCELLENT: ZVI proven in PRBs at multiple sites; concern regarding generation of ammonia from nitrate	EXCELLENT: Expected to last for decades	[2]MEDIUM: \$1650/kg Cr(VI) reduced, \$2/1000L water treated; \$5000/m barrier
Nano-scale Iron	EXCELLENT: Nano-scale ZVI proven to reduce Cr(VI) in the field; higher chromate reduction capacity per gram of iron	GOOD: Potential delivery as a slurry; in situ delivery demonstrated at field pilot scale; radius of influence uncertain	EXCELLENT: Stable slurry; requires proper handling	EXCELLENT: ZVI proven in PRBs at multiple sites; concern regarding generation of ammonia from nitrate	EXCELLENT: Expected to last for decades	[2]HIGH: \$2750-5500/kg Cr(VI) reduced, \$3.5-7.0/1000L water treated; \$9000-18,000/m barrier
Biological Substrate	GOOD: Effective in field and laboratory for reducing metals; long-term effectiveness uncertain as stand alone reductant	EXCELLENT: Potential delivery as a liquid, similar to CaS_5	EXCELLENT: Benign, biodegradable and non-toxic	EXCELLENT: High acceptability	POOR: Continuous or multiple injections necessary; recirculation possible; biofouling potential problem	[3]LOW: insignificant relative to CaS_5 or iron; \$0.04-0.35/1000L water treated

[1] Assumes Cr(VI) reduction occurs via eq 1, S^0 has no residual reduction capacity, 8.4 mg/L DO, 1.29 mg/L Cr(VI), and 58.8 mg/L NO_3^- converted to N_2 gas, and a cost of \$2-3/gallon for CaS_5; [2] Assumes Cr(VI) reduction occurs via eq 3, H_2 evolved cannot reduce Cr(VI). It is assumed that micron-scale iron and nano-scale iron can reduce the same mass of Cr(VI). In all cases it is assumed that all the reductant is fully utilized to reduce all oxidants present in Hanford groundwater (Table 3.2 assuming $NO_3^- \rightarrow NH_4^+$); [3] Assumes 8.4 mg/L DO, 1.29 mg/L Cr(VI), 58.8 mg/L NO_3^- converted to N_2 gas and 75% of total electrons available are utilized for reduction of oxidants and 25% go into biomass production

4.0 REMEDIAL STRATEGIES

Information in this section of the report addresses the project's objective of evaluating the most practicable means of introducing chemical/biological amendments in the target zones along the current ISRM barrier.

4.1 Passive Barrier Mending Considerations

The passive barrier was designed and approved as an interim remedy to capture and treat Cr-contaminated groundwater, thereby mitigating potentially adverse ecological impacts to the river system. The long-term effectiveness of the barrier is determined by the total mass of reductant emplaced in the treatment zone and the mass flux of oxidants through the treatment zone per unit time. The observed premature breakthrough of Cr(VI) in barrier wells has been attributed to physical and chemical heterogeneities in the aquifer and unexpectedly high concentrations of competing oxidants in the groundwater. Table 3.4 provides an estimated range of barrier longevities based upon aquifer hydrogeology and redox chemistry when dithionite is used. Barrier maintenance costs will be much higher than previously estimated due to the observed premature breakthrough.

One approach to maintenance of barrier effectiveness is frequent reinjection of dithionite or another liquid reductant, such as CaS_5. Another alternative is delivery of a solid chemical reductant, such as ZVI, within the high-conductivity zones in the aquifer. However, without good characterization of the location and extent of the high-conductivity zones, design of a system for delivery of ZVI to these targeted zones cannot be compared to the proven delivery of liquid reductant throughout the aquifer. In addition to aquifer characterization to delineate high-conductivity zones, laboratory testing to compare the various liquid and solid reductants must be completed before a preferred alternative can be selected.

The TAT believes that no amendment can provide the assurance of Cr(VI) remediation for an extended time (> 20 years) when employed in a passive design, without frequent reinjectiion along the barrier or active source and/or plume control. Due to the lack of information on the source location and extent, it is unclear how long the barrier would need to be in place. Without that information, it is difficult to assess the costs of various remedial options. Bench- and field-scale testing would be required to quantify the feasibility and cost effectiveness of approaches for mending the barrier. Transitioning to an active, in situ remedial approach may provide benefits of a shorter treatment period and life-cycle cost savings.

4.2 Active Remedial Strategies

Considering the recent performance of the passive barrier, the TAT believes that simple mending of the barrier with alternative amendments without containing/treating the source and delineating the extent of the Cr(VI) plume requiring treatment may not likely be a reliable long-term remedial solution. It is currently not possible to provide a reasonable estimate of the required lifetime of the barrier due to a lack of information on the mass and extent of the source and the dissolved plume. Project management schedules at Hanford reflect the agreement between DOE and the regulators to have a final ROD in place for Cr source and plume treatment by 2012.

One objective in monitoring barrier performance for the Interim ROD was to provide scientific information for selection and design of a reliable final remedy. The TAT believes that sufficient performance data now exist to support evaluation of altering the design of the interim remedy.

Experience gained at numerous pump-and-treat sites indicates that approximately 50 pore volumes must be flushed through the aquifer to achieve suitable water quality, assuming the source is controlled (Jim Rouse, Personal Communication). This large number of pore volumes is required because of aquifer heterogeneity, the presence of secondary precipitates, and sorption of the contaminant of concern onto aquifer solids. The cleanup of the Area 100-D Cr(VI) plume is further exacerbated by:

- the continued presence of a source term, as yet undefined, likely present in both the vadose and saturated zones,
- seepage from the 182-D reservoir, which has shifted ground-water flow lines, and
- periodic reversal of ground-water flow as a result of high river stage.

Therefore, it is the opinion of the TAT that a more active remedial approach will be required as a part of the final remedial approach (Rouse, 2004A). Such an active approach is not without certain technical issues, discussed in the following paragraphs.

Source Definition

In general terms, the source of the Cr(VI) is believed to have resulted from spills or leaks during unloading and handling of the corrosion inhibitor, supported by the elevated concentrations in the groundwater. Location of the actual source in the 100-D Area is a challenging task and delineation would not be cost-effective. However, a source-treatment approach used at many large, complex sites is based upon gridding the potential source area with shallow, inexpensive infiltration galleries, where the infiltrating solutions can follow the pathway of the original contaminant source.

Limited investigations in the 100-D Area to define the source consisted of leaching soil cores with groundwater to measure soluble Cr(VI). This approach is preferred over analysis of total Cr in soil cores. However, shallow soil sampling to define the source area is cost prohibitive and may not likely find the source.

Effects of Fluctuating Groundwater Flow Direction

On-site personnel recognize the difficulties resulting from changes in flow direction due to seepage from the 182-D Reservoir and from high stages in the Columbia River.

Secondary Chromate Minerals

Precipitation of secondary Cr(VI) minerals in the vicinity or down-gradient of the source area may complicate the situation. However, active treatment within the source area and groundwater plume should address this problem.

4.2.1 Source Treatment with Passive Barrier

Addition of active source treatment to the mending of the passive barrier could be considered a final remedy for the 100-D Area. Recognizing that the source area is poorly defined, a grid of infiltration galleries buried in a series of trenches covering the potential source area could provide an active treatment component to the system. Reductant-bearing solution would be introduced into the pipes and allowed to percolate through the subsurface.

Infiltrating solutions would displace a portion of the Cr(VI) present in the unsaturated zone to the saturated zone, but much of the Cr(VI) would be reduced to the trivalent form and fixed in place by reaction with the reductant. Once the reductant reaches the water table, it would then advance downgradient, reacting with and reducing residual Cr(VI) in the saturated zone. Obviously, the advance of the reductant through the vadose and saturated zones will result in reaction and consumption of the reductant, such that a reaction front will advance more slowly than an actual particle of water applied in the infiltration trenches.

Water for the infiltration can be obtained from treated effluent from the existing pump & treat system or from river or potable water. It would be dosed with the selected reductant and discharged into the galleries. Because many reductants are photosensitive and also would tend to react with atmospheric air, the infiltration galleries should be designed to minimize atmospheric exposure.

Selection of the reductant must carefully consider site geochemistry (Blessing and Rouse, 2002; Rouse, 2004B). Use of ZVI is not likely to be appropriate for this part of the system, although it should be tested. Dithionite likely is too reactive for this application and it would produce elevated SO_4^{-2} concentrations in the groundwater. Polysulfide has been successfully applied in a ten-acre infiltration basin in Colorado and in smaller infiltration basins and grids in California, Indiana, and South Australia (Rouse and Davies, 2000; Thomasser and Rouse, 1999). Thus, polysulfide offers the highest potential for active source-zone remediation.

In conjunction with source treatment, the current ISRM barrier could be operated in the passive mode, most ideally by ZVI introduction in preferential flow paths.

4.2.2 Source Treatment with Active Hydraulic Control and Treatment in the Barrier Wells

Another option for active remediation is the addition of hydraulic control and active treatment in the barrier wells, along with the source-zone treatment. This option has the potential to reduce the time needed to achieve closure. Because the barrier wells are installed as a staggered line, water could be pumped from the downgradient and injected into the upgradient wells along the barrier. Water pumped from the barrier wells would be amended with reductant and either injected into upgradient barrier wells or injected in source-zone infiltration galleries. Monitoring and modeling would be needed to establish the operational parameters.

4.2.3 Source and Plume Treatment with Active Hydraulic Control and Treatment in the Barrier Wells

The most robust active-treatment system utilizes all of the features of the previous system (source treatment, hydraulic control and treatment in the barrier wells) along with active treatment of the groundwater plume. The added cost of this system could be deemed appropriate by significantly reducing the life-cycle cost for remediation of the problem. Groundwater from wells in the core of the groundwater plume (possibly some of the existing pump and treat wells) would be treated with reductant and reinjected along the margin of the plume and into the infiltration galleries in the source area.

Experience at several sites (Thomasser and Rouse, 1999) indicates that approximately 2 to 3 pore volumes must be flushed through the aquifer to achieve remediation goals using such an active system. Thus, while the capital and operating costs would be significantly higher during operation, they would likely be offset by the fact that the system would only need to operate for a few years, rather than decades to centuries needed for less active systems.

4.3 Performance Monitoring

Key performance monitoring metrics that should be adopted for evaluating alternative amendments and remedial strategies, include the following:

- comparison of post-emplacement groundwater quality with baseline groundwater quality in the treatment zone;
- groundwater quality analysis of upgradient and downgradient monitoring wells following emplacement;
- solid-phase analysis on sediment cores recovered from the treatment zone to estimate barrier longevity and provide information on reaction byproducts and solid-phase conversions;
- hydraulic testing to assess possible changes in aquifer hydraulic properties;
- microbiological analysis to evaluate the potential impact of microbial iron and sulfate reduction; and
- evaluation of potential secondary effects of the ISRM technology.

5.0 TESTING AND EVALUATION OF POTENTIAL REMEDIAL STRATEGIES

5.1 Recommended Parameters to Be Tested

Both laboratory and field testing of potential amendments must be conducted so that a comparative analysis, including cost-benefits, can be completed before a preferred amendment can be selected. Laboratory bench-scale studies, and pilot-scale investigations are needed to determine the effectiveness, longevity, and methods to implement the amendment prior to final selection:

- Effectiveness refers to the ability of an amendment to reduce Cr(VI) to less than 20 μg/L, thereby protecting ecological receptors downstream of the barrier. For a treatment technology to be effective, it must also be demonstrated that toxic reaction products are not produced;
- Longevity refers to the ability of an amendment to retain sufficient reducing capacity to continue to be effective for a specific duration under reaction conditions; and
- Implementability refers to the ability to deliver the amendment in the subsurface using the existing infrastructure, and to keep the amendment in place after delivery.

Estimates of the amendment mass required for creating a passive redox barrier using the existing wells and the lifetime of the amendment, can be calculated using the conceptual model depicted in Figure 5.1. The conceptual model assumes a steady input of oxidant based on: 1) the site groundwater chemistry (DO, Cr(VI), and NO_3^-), and 2) the premise that all DO and Cr(VI) are reduced and that NO_3^- is transformed to N_2 (CaS_5 and biological reduction) or NH_4^+ (Fe^0). This is a conservative estimate, because it represents the maximum possible oxidant loading and maximum reduction products (unless otherwise noted). It also assumes a saturated thickness of 4.6 m, and a porosity of 0.14. In the absence of data regarding the spatial heterogeneity of the formation, the estimates must be "average" estimates for the formation. It is acknowledged that this could lead to gross errors regarding barrier performance and amendment lifetime, however, this approach allows for the comparison of cost between amendments on a per kg Cr(VI) reduced, or per m of barrier length. Also as a point of reference, Appendix D provides a recommended procedure for estimation of the lifetime of various amendments when sufficient aquifer characterization data and laboratory treatability data are available.

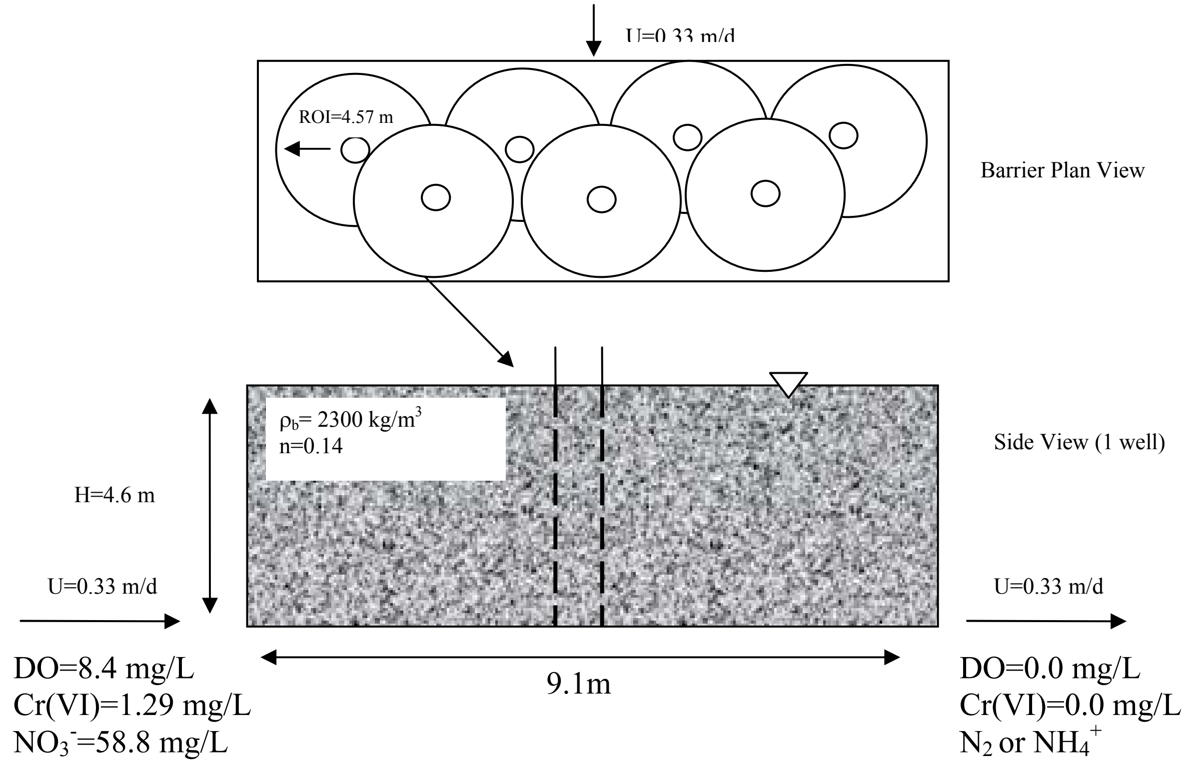

Figure 5.1. Barrier Conceptual Model

5.2 Recommended Laboratory Treatability Testing

CaS_5 and ZVI have both been demonstrated to effectively reduce Cr(VI) in the field. Many factors affecting the effectiveness, longevity, and implementability are site specific and require bench- and field-scale evaluations in Hanford sediment and groundwater. The key variables requiring laboratory treatability testing are: 1) the reducing capacity of each amendment in the aquifer matrix, 2) the rate of Cr(VI) reduction under in situ conditions, and 3) the lifetime of the amendment. Other variables include the reaction products and the stability of reduced Cr(VI) species formed. The recommended treatment parameters and potential methods to evaluate each parameter are summarized in Table 5.1. Details of the testing are described in the remainder of the section by parameter to be determined.

Table 5.1. Treatability Testing Parameters for Calcium Polysulfide, Nano-Scale Iron, and Micron-Scale Iron

Recommended Treatment Parameters	**Performance Metrics**	**Method of Evaluation/Measurements**		
		Batch	Column	Field
Effectiveness	Rate of Cr^{6+} reduction in aquifer per unit mass of amendment	Cr(VI), O_2, NO_3^-, SO_4^{2-}, HS^-, S^o, Fe(II) pH, ORP		
	Identify reaction products	NO_2^-, NH_4^+ (for Fe^0), Cr(VI), CaS_5 reaction products		
	Speciation and stability of Cr^{3+} precipitates formed	Cr-containing precipitates using XRD, SEM, TEM, EXAFS	Desorption to evaluate stability	
	Ability to treat source zone	High Cr(VI) concentrations	Evaluate vadose zone delivery methods	
<u>Longevity</u>	Amended sediment reduction capacity, lifetime, and deactivation	Total Cr(VI) reducing power of amended Hanford sediment (Walkley-Black method[1,2])	Cr(VI), O_2, NO_3^-, SO_4^{2-}, HS^-, S^o Fe(II) pH, ORP, and H_2 in column influent/effluent	
	Relationship between reduction capacity, S_R, and hydraulic conductivity, K		Measure reduction capacity in sediments with different K to correlate S_R and K	
	Measure anaerobic corrosion rates (i.e. hydrogen production rates) in the presence and absence of DO and nitrate	H_2, Fe^0, Fe(II)		

	Species responsible for residual reduction potential (for calcium polysulfide)	ORP vs. time, monitor S^0, HS^-, SO_4^{2-}, XRD, SEM, TEM, EXAFS		
Implementability	Methods to deliver reductant		Iron mobility vs. flow velocity in low K and high K materials, distribution of Fe^0, mass Fe^0/unit volume, effect of shear thinning fluids	Iron mobility vs. flow velocity in low K and high K materials, distribution of Fe^0, mass Fe^0/unit volume, monitor amendment in adjacent wells to determine the ROI
	Reductant mobility after placement		Fe^0 and CaS_5 exiting column vs. time in Hanford sediment under natural groundwater flow conditions	Fe^0 and CaS_5 in downstream monitoring wells
	Pore plugging potential		Permeability vs. time after amendment addition	Aquifer permeability
	Radius of influence/Fate of amendments			Monitor for reaction products/amendments in downstream monitoring wells, monitor rate of re-oxidation of immobilized Cr(III)

[1] Walkley, A., Black, L. A., Soil Science, 37:29-38, 1934; [2] Bartlett, R. J., James, B. R., Mobility and bioavailability of chromium in soils. In, Chromium in the natural and human environments, Vol. 20, J.O Nriagu and E. Nieboer, eds. John Wiley and Sons, New York: 267-30

5.2.1 Effectiveness

C(VI) reduction rate. The rate at which each amendment reduces Cr will determine the effectiveness of that particular amendment. Considering a treatment zone length of roughly 20m, and a groundwater flow rate of 0.3m/day, the rate of Cr(VI) reduction must be rapid enough such that all the Cr is reduced in ~60 days. Kinetics will not be an issue with either CaS_5 or ZVI. Batch tests described in Table 5.1 are recommended. These tests will consider groundwater (e.g. O_2, NO_3^-) and amendment (Fe^{2+}, SO_4^{2-}, HS^-, etc.) chemistry in assessing the rates. Empirical rate equations for each amendment can be determined using these tests.

Identify reaction products. The primary reaction products of potential concern during CaS_5 application are Fe(II), Mn(II), and As(V)/As(III), which are typically mobilized under reducing conditions, and the oxidized sulfur species (S^0, SO_4^{2-}) formed during the reaction. Arsenic is the only constituent that is generally considered toxic to downstream receptors. Arsenic, along with Fe and Mn, have been detected in elevated concentrations in the aquifer within the ISRM treatment zone.

The stoichiometric conversion of NO_3^- to NH_4^+ by ZVI has been demonstrated in the laboratory. It is possible that the reduction of NO_3^- (~58.8 mg/L) in Hanford groundwater by ZVI will lead to high concentrations of NH_4^+ (~ 17 mg/L) in groundwater discharging to the Columbia River. The toxicity of NH_4^+ to aquatic species, including juvenile salmonids, is well documented. It is therefore necessary to assess the amount of NH_4^+ formed during ZVI treatment of Hanford groundwater and the attenuation capacity of the aquifer matrix. This should be done using bench-scale batch and column tests, prior to testing in field-scale pilot tests.

Speciation and stability of Cr(III) precipitates formed. The speciation and stability of reduced Cr using ZVI has been well documented and requires no further assessment. The composition of reduced solid phase Cr species produced using CaS_5 as a reductant has not been well documented, but field tests have not shown significant Cr(VI) rebound, suggesting that reduced Cr is stable and unlikely to remobilize. Batch and column tests using Hanford sediment, groundwater, and CaS_5 should verify the stability of reduced Cr species. Some estimation of Cr(VI) concentrations that may be attained as the reductant is consumed and the barrier re-oxidized should be provided.

Ability to treat the Cr(VI) source zone. CaS_5 could potentially be used to treat the source zone for the active remediation scenario. CaS_5 has been used for source-zone treatment in the saturated zone at a number of field sites. It is unclear if CaS_5 can maintain reducing conditions and effectively reduce Cr(VI) in the unsaturated zone. Batch tests using high Cr(VI) concentrations in Hanford sediment can be used to assess the rate and capacity of each amendment. Column tests, in unsaturated Hanford sediment, could be conducted to assess the amendment delivery and effectiveness of source-zone treatment for each amendment.

5.2.2 Longevity

For a passive barrier system, the longevity of a treatment technology is a function of the total mass of reductant emplaced in the aquifer and the total mass flux of oxidants moving through the barrier in a given time, as described by equations 1 and 2 in Appendix D. For an active treatment system, the longevity is less of a concern than the effectiveness because amendment will continually be added to the system.

Amendment reduction capacity, lifetime, and deactivation rate. The reduction capacity of amended Hanford aquifer will determine the longevity of the treatment technologies. The greater the reducing capacity that can be imparted on aquifer sediments per application, the longer the barrier can retain the ability to reduce Cr(VI). The reduction capacity of each amendment can be determined using simple batch tests measuring the total reducing capacity of the amended sediment. At least three replicates should be used to estimate the mean and standard deviation. The total reducing capacity of the amendments may not be utilized if the reaction rates are significantly slowed. The lifetime (i.e. residual reducing capacity) of CaS_5 is unknown so the rate of delivery cannot be determined a priori. For iron, the surface of the iron may be passivated such that it loses its ability to reduce oxidants present in Hanford groundwater and therefore its effectiveness. Long-term column tests (designed to mimic decades of treatment) using Hanford sediment amended with either Fe^0 or CaS_5 are recommended.

The ability of the amendment to continually reduce Cr(VI) can be monitored by measuring NO_3^-, O_2, and ORP in the influent and Cr^{6+}, NO_3^-, NO_2^-, NH_3, O_2, and ORP in the effluent during flushing with Hanford groundwater. The rate of deactivation can be monitored in these experiments to determine if the Cr(VI) reduction rate slows to a point where the barrier operation time (Δt_{req}) becomes longer than the groundwater retention time in the barrier.

Because the Hanford Formation is heterogeneous, it is desirable to measure the Cr(VI) reducing capacity, S_R, as a function of the hydraulic conductivity, K. This can be done by measuring the rate of Cr(VI) reduction, K, and S_R for a column filled with amended Hanford sediment, and correlating these parameters.

Anaerobic Fe^0 corrosion rate. For a ZVI amendment alternative, the iron corrosion rate in Hanford groundwater must be determined in order to assess its longevity. Iron will reduce H^+ to form H_2. This hydrogen-gas production is essentially wasting electrons if the resulting H_2 cannot be used in some manner to reduce Cr(VI), and it limits the ability of ZVI to reduce the Cr(VI). It is expected that H_2 production will be initially rapid, and then decrease to some slow steady-state rate. This H_2 generation rate will potentially be more rapid for nanoscale iron than micron-scale iron, because of its higher surface area/reactivity. Batch and column tests using Hanford groundwater and sediment should be conducted to determine the fraction of Fe^0 that is wasted for H_2 generation, and to determine if the H_2 generated can be used for Cr(VI) reduction (probably will be biologically mediated).

Species responsible for residual reduction capacity. For CaS_5, there is evidence in field tests that CaS_5 can provide residual reducing capacity, but the species responsible for this is unclear. Knowing this species could provide a means to rapidly assess the residual reducing capacity in the aquifer after amendment addition. Batch tests monitoring ORP as a function of time after CaS_5 addition should be conducted to monitor the longevity of reducing conditions. The reduced species responsible for the residual reduction capacity (e.g. HS^-, S^0) should be identified, perhaps using a combination of powder x-ray diffraction with microscopic and spectroscopic techniques, such as scanning electron diffraction, transmission electron microscopy, energy dispersive x-ray spectroscopy, extended x-ray absorption fine-structure spectroscopy.

5.2.3 Implementation

Methods to deliver reductants. CaS_5 is a liquid, has been demonstrated in the field, and can probably be easily delivered using the existing barrier wells. Delivering micron-scale and nano-scale iron is less proven, although two field demonstrations with nano-scale iron have shown that it can be delivered in situ via gravity feed into treatment wells. Methods to deliver micron-scale iron have been evaluated at PNNL (DOE, 2004). Laboratory column studies using Hanford sediments and groundwater should be conducted to determine delivery conditions (e.g. injection velocity) required to achieve an acceptable radius of influence and to estimate what the resulting iron distribution will be in the subsurface. These studies should be done in both high K and low K sediments.

Reductant mobility/fate after placement. The ZVI delivered must remain in place in order to provide long term reducing capacity in the treatment area. Therefore, column and field tests must be conducted to assess the mobility of iron placed under normal groundwater flow conditions. This is more of a concern for nano-scale iron than for micron-scale iron as the larger particle size of micron-scale iron will limit its mobility after placement. This limited mobility, however, also makes it more difficult to deliver and shear thinning fluids or some other technique must be used to enhance iron transport into the aquifer.

5.3 Field Testing

During the evaluation and treatability testing of the present ISRM barrier rigorous methods were employed to validate ISRM performance and implementability and help predict barrier longevity, as described in the previous TAT report (DOE, 2004). This same rigorous approach should be followed for evaluating alternative amendments and remedial strategies, and include the following.

- Post-amendment groundwater quality should be compared with baseline groundwater quality in the treatment zone and in upgradient and downgradient monitoring wells to assess barrier performance and potential loss of reductant; (testing should be conducted in areas that are showing signs of premature breakthrough). It will be critical to assess, in addition to those analytes previously monitored, nitrogen compounds (NO_3^-, NO_2^-, N_2, and NH_3) such that an accurate picture evolves as to total groundwater oxidation potential and potential ecological impacts of nitrogen transformations. Several multilevel monitoring wells could be installed immediately downgradient from the treatment zone, such that the reaction front can be monitored to provide information crucial to development of a fate and transport model. Field monitoring parameters should also include ORP measurements, as well as the current use of DO as an indicator parameter. Monitoring of ZVI performance should also include in situ H_2 measurement, which will provide real-time indicator of the ZVI reactivity.
- Solid-phase chemical, physical, and microbiological analysis of sediment cores recovered from the treatment zone should be conducted to estimate barrier longevity and provide information on reaction byproducts and solid-phase conversions. Pretest cores should be

analyzed for reactivity as was previously conducted during dithionite treatability studies. Post-treatment cores should be analyzed for residual Fe^0 (if micron- or nano-scale ZVI is used), Fe(II) phases, and Cr phases. Evaluation of the mass and reactivity of emplaced ZVI should include measurement of ORP within core sections and direct measurement of the mass of Fe^0 remaining in residual particles. Special analysis for solid sulfur species (e.g. S^0) should be considered when polysulfide is being evaluated to factor into mass balance calculations and verify reaction byproducts. Microbiological analyses should be conducted to verify the role that SRBs and other dissimilatory metal-reducing bacteria (DMRB) are playing in removing sulfate and reducing iron and manganese oxyhydroxides within and downgradient from the treatment zone. These analyses can be conducted with various microbiological techniques, which might include quantitative enrichments, polymerase chain reaction (PCR) and or quantitative PCR, and physiological methods, such as, phospholipid fatty acid (PLFA) analysis.

- Solid-phase analysis of cores should include testing that evaluates the deposition and stability of reaction byproducts. Particular attention should be given to assessing the stability of precipitated sulfur species. Previous use of calcium polysulfide at Cr-contaminated industrial sites indicates that elemental sulfur is precipitated (Personal Communication with Jim Rouse). Numerous bacteria derive energy to support growth from the oxidation of sulfur according to the Eq. 7.

$$S^0 + H_2O + 1\tfrac{1}{2}O_2 \rightarrow SO_4^{-2} + 2H^+ \qquad (7)$$

- A potential concern with the emplacement of ZVI is the stoichiometric conversion of NO_3^- to NH_4^+ (Till et al., 1998). In this regard, it will be critical to monitor nitrogen transformations in these systems and also evaluate the capacity of down-gradient soils to attenuate NH_4^+ migration.
- Hydraulic testing should be conducted to determine the distribution of hydraulic conductivity and assess possible changes in aquifer hydraulic properties as a result of lixiviant addition. Testing should include constant-rate discharge and tracer tests, along with Electronic Borehole Flowmeter (EBF) analysis.
- A new “passive flux meter” (PFM) to provide depth-discrete, time-integrated estimates of contaminant and fluid flux within and outside the barrier should be tested (Annable et al., 2003; Hatfield et al., 2002; Hatfield et al., 2003; Klammler et al., 2003). Further information about the PFM is provided in DOE (2004). Down-gradient measurements can be used to estimate the cumulative Cr(VI) flux emanating from the barrier. Up-gradient measurements can be made to estimate the Cr(VI) mass loading into the reactive barrier. The difference in the response between the upgradient and downgradient PFMs could be attributed to the treated mass of Cr.
- Amendment injection testing to assess delivery into the aquifer.
- Single-well push-pull testing to determine in situ rates of reduction and in situ reduction capacity.

Specific recommendations related to field-testing are provided in Table 5.2 showing treatment parameters measured for each of the proposed tests. Table 5.1 also shows recommended field parameters to be tested as related to implementability.

If source treatment or source and plume treatment remedial strategies are implemented, monitoring of all upgradient wells should also be conducted so that the contaminant mass flux and treatment efficiency can be estimated to predict the time required for source-term removal. Source-zone treatment should result in decreasing concentrations of Cr(VI) in all upgradient wells located within the Cr(VI) plume. Multiplying the average Cr(VI) concentrations for all upgradient wells by an approximate aquifer volume will provide a estimate of the total mass of Cr(VI) in the aquifer and this mass should be decreasing with time if the source-zone treatment is effective.

Table 5.2. Field Test Parameters

Field Test	Treatment Parameters	Issue	Approach
Hydraulic Testing of Existing Wells	Changes is K due to amendments $\ln \overline{K}, \sigma_{\ln K}$	Longevity, Implementation	Rising/falling head tests, Constant head tests, Flow meter tests. Tests should be both prior to and following addition of amendments.
Injection of Amendments	Rate of transport of reductant, Changes in permeability	Longevity, Implementation	Injection tracer test of reactive and conservative tracers
Single-Well Push-Pull Test	In-situ rate of Cr(VI) reduction, In-situ reduction capacity, mobility of reductants under reductants folllowing addition of amendments.	Effectiveness, Longevity	Create relatively small treatment zone about a well then inject, noncontaminated groundwater amended with a conservative tracer. Measure pH, temperature, [Fe(II)], ORP, S(-II), DO, Cr(VI), turbidity, temperature in the field. Collect samples to be analyzed in the laboratory for NH_4^+, NO_{3-}, NO_{2-}, SO_4^{2-}.
Barrier Monitoring	Barrier Performance, Loss of reductant (Fe(II)) with time/reduction cycle	Effectiveness, Longevity	Standard groundwater monitoring practices. Measure pH, temperature, [Fe(II)], ORP, S(-II), DO, Cr(VI), turbidity, temperature in the field. Analyze samples in the laboratory for NH_4^+, NO_3^-, NO_2^-, SO_4^{2-}.

5.4 Preliminary Cost Estimates

Without preliminary data regarding the total reduction capacity of the sediment following application of each amendment (i.e. the number of electrons from each amendment that is used to reduce oxidants present in Hanford groundwater), firm cost estimates for each amendment are not possible. However, at the request of Fluor Hanford and in the absence of detailed site characterization data, preliminary relative costs for each of the recommended amendments are estimated by making some simplifying assumptions about the Hanford Formation and associated aquifer, and about the efficiency of each amendment. Costs for dithionite were not included in this analysis. However, Fluor should have actual costs for dithionite that could be compared to those for the alternative amendments described below. It is anticipated that the costs for dithionite would likely exceed those of CaS_5, an alternative liquid amendment that could be delivered in a similar fashion to dithionite. This conceptual model (Figure 5.1) includes the following general assumptions. Other assumptions specific to a given amendment are provided in each sub-section[2].

- Hanford groundwater upgradient of the ISRM barrier, on average, contains the following concentrations of oxidants: DO, 8.4 mg/L; NO_3^-, 58.8 mg/L; and Cr(VI), 1.29 mg/L.
- The radius of influence of each barrier well is 4.57 m.
- The saturated depth of the formation is 4.57 m.
- Groundwater velocity is 0.33 m/d (1 ft./day)
- Formation porosity is 0.14 and soil bulk density is 2.3 g/cm^3 (assumes a homogeneous aquifer, which is known to introduce tremendous uncertainty).
- All amendments are 100% utilized.
- Electrons available in each amendment are only used to reduce DO, NO_3^-, and Cr(VI), except where noted.
- Kinetics of reduction are sufficiently fast to be ignored.

As described in section 3.2, the amendment costs are presented in two different ways, $/kg Cr(VI) reduced and $/m3 groundwater treated. For amendments that can be used to mend the current ISRM barrier, a $/m of barrier yr lifetime is also calculated. These estimates assume that the amendment will be introduced into the barrier uniformly over the entire saturated depth of the aquifer. Table 5.3 provides a summary of the cost for each amendment. Note that the upper end of cost and the lower end of the estimated barrier lifetime are conservative estimates. Two estimates of oxidant demand are included to show a range of possibilities: 1) highest possible oxidant loading with reduction to the furthest extent possible and 2) low oxidant demand (3.0 mol e-/m3). It is possible, and likely, that there will be fewer oxidants present in the groundwater, or that each oxidant will not be fully reduced to the maximum extent possible. It should also be noted that the estimated lifetimes are highly sensitive to choice of groundwater velocity similar to the dithionite example provided in Table 3.4. This parameter should be carefully considered in future studies.

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[2] Aquifer values for bulk density and porosity represent average properties based on Williams et al. (2000)

5.4.1 Calcium Polysulfide

The cost of CaS_5 is calculated assuming that the sulfur in CaS_5 is oxidized to elemental sulfur according to equation 1 in Section 3.1.2. Based on this assumption, CaS_5 provides two electron-equivalents/mole. For Hanford groundwater, it is assumed that CaS_5 reduces DO to water, and NO_3^- is to N_2, in addition to Cr(VI). Based on these assumptions, there are ~5.9 electron equivalents of oxidants per m^3 of Hanford groundwater (Table 3.2). Considering a 29 wt% solution of CaS_5, each m^3 of solution contains 2900 mol electron equivalents available to reduce oxidants in Hanford groundwater. Using a current price of \$530-\$784/m^3 of a 29 wt% CaS_5 solution, the cost to treat each m^3 of Hanford groundwater is estimated at \$1-\$1.6/m^3 treated. At a Cr(VI) concentration of 1.29 mg/L, this equates to \$800 to \$1000/kg Cr(VI) reduced or immobilized. For the lower oxidant loading, these costs decrease by a factor of two (Table 5.3).

Table 5.3. Summary of Amendment Costs

Calcium Polysulfide (CaS_5)

	CaS_5 (\$530/m^3 29 wt% solution)		**CaS_5 (\$784/m^3 29 wt% solution)**	
Cost and Estimated Lifetime	Low oxidant demand (3 mol e^-/m^3)	High oxidant demand (5.9 mol e^-/m^3)	Low oxidant demand (3 mol e^-/m^3)	High oxidant demand (5.9 mol e^-/m^3)
\$/kg Cr(VI reduced)	400	800	600	1200
\$/m^3 water treated	0.5	1.0	0.8	1.6

Micron-scale Iron

	Fe^0 (\$13.2/kg)	
Cost and Estimated Lifetime	Low oxidant demand (3 mol e^-/m^3)	High oxidant demand (8.7 mol e^-/m^3)
\$/kg Cr(VI reduced)	570	1650
\$/m3 water treated	0.73	2.0
\$/(m barrier yr lifetime)	60	150
Lifetime (yr)	50[1]	16.5
Pore volume treated (PV/m barrier=6 m3)	630	220

[1] The actual lifetime will depend on the corrosion rate of Fe to form H_2 (i.e. the lifetime).

Nano-scale Iron

	Fe^0 (\$22/kg)		**Fe^0 (\$44/kg)**	
Cost and Estimated Lifetime	Low oxidant demand (3 mol e^-/m^3)	High oxidant demand (8.7 mol e^-/m^3)	Low oxidant demand (3 mol e^-/m^3)	High oxidant demand (8.7 mol e^-/m^3)
\$/kg Cr(VI reduced)	950	2750	1900	5500
\$/m3 water treated	1.2	3.5	2.4	7.0
\$/(m barrier yr lifetime)	95	275	190	550
Lifetime (yr)	50[1]	16.5	50	16.5
Pore Volumes Treated	630	220	630	220

[1] The actual lifetime will depend on the corrosion rate of Fe to form H_2 (i.e. the lifetime).

Organic Amendments (Lactate)

	Dextrose ($0.35/lb)		Lactate ($1/lb 60 wt% solution)	
Cost and Estimated Lifetime	Low oxidant demand (3 mol e^-/m^3)	High oxidant demand (5.9 mol e^-/m^3)	Low oxidant demand (3 mol e^-/m^3)	High oxidant demand (5.9 mol e^-/m^3)
$/kg Cr(VI reduced)	15	31	140	270
$/m3 water treated	0.02	0.04	0.18	0.35

While it is likely that metal sulfides and elemental sulfur resulting from CaS_5 injection will provide residual reducing capacity, the species responsible for residual reducing capacity and the lifetime of such species are unknown. Laboratory and field evaluations of CaS_5 could provide some insight into this, but at this time, there is too much uncertainty in the longevity to make a reasonable estimate of the lifetime for CaS_5.

5.4.2 Micron-Scale Iron

Based on equation 3 in Section 3.1.3, Fe^0 provides 3 electron equivalents/mole for reducing Cr(VI), i.e. $Fe^0 \rightarrow Fe^{3+}$. The rate of corrosion of Fe^0 to form H_2 has been documented (Reardon, 1995). The average corrosion rate for iron was ~0.5 mmoles/kg-d. Converting the units of kg iron to moles, one gets a rate constant of 2.8×10^{-5} d^{-1} for granular iron with a surface area of 1.5 m^2/g. This corresponds to a half-life of ~68 years. Assuming a surface area for nano-scale iron of 23 m^2/g, the estimated H_2 generation rate is ~4.3×10^{-4} d^{-1} with a half-life of 4.4 years. A rate of H_2 generation of ~1.2 mmol H_2/kg-d was measured for Fe^0 nanoparticles supplied by Toda, America, Inc. (Arlington Heights, IL) (Liu at al., 2004). This corresponds to a half-time of ~28 years. The Toda iron has a measured surface area of 23 m^2/g.

The iron lifetime is a critical parameter for estimating the barrier longevity; bench scale testing must be performed to accurately determine the H_2 generation rate. Fortunately, it is likely that any H_2 formed will be utilized by microbes to reduce oxidized species in Hanford groundwater. Thus, for these estimates it is assumed that each mole of Fe^0 will provide 3 moles of electron ($Fe^0 \rightarrow Fe^{3+}$). For Hanford groundwater, it is assumed that Fe^0 also reduces DO to water, and NO_3^- is reduced to NH_4^+, in addition to reducing Cr(VI). Based on these assumptions, there are ~8.7 mol electron equivalents of oxidants per m^3 of Hanford groundwater (Table 3.2). Using a current price of $13.2/kg Fe^0, the cost to treat each m^3 of Hanford groundwater is estimated at $2/$m^3$. At a Cr(VI) concentration of 1.29 mg/L, this equates to $1650/kg Cr(VI) reduced/immobilized, or a cost of $150/(m barrier yr lifetime). If evolved H_2 is in fact not utilized, these costs would be three times higher.

For these estimates, it is assumed that enough Fe^0 is delivered to fill roughly 0.5 volume % (0.2 wt% of sediment) of the void fraction of the Hanford Formation. Note that this is ONLY A ROUGH ESTIMATE. Bench-scale and pilot-scale treatability tests will have to be conducted to accurately determine their actual values. This current estimate provides ~4.9 kg of Fe^0/m^3 of the aquifer, and therefore the capacity to treat ~220 pore volumes (9,200 m^3 of groundwater per well). Assuming a groundwater flow of 0.33 m/day, the barrier longevity is estimated to be 16.5 years. If only one-mole electrons per mole Fe^0 were available, the barrier longevity for this amount of Fe^0 would be lower by a factor of three. The barrier lifetime is linearly correlated to the mass of Fe added and groundwater velocity (e.g., Table 3.4). It is also important to note that this is a conservative estimate assuming that all of the oxidants present in Hanford groundwater are reduced to the fullest extent, and that the groundwater is saturated with O_2. It is likely that the DO levels will be less that saturated, and that complete oxidation of all constituents will not occur. Assuming a lower total oxidant loading, e.g. 3 mol e-quivalents/m^3, will lower costs and increase lifetimes by a factor of ~3, and extend the barrier lifetime to ~50 years. If Fe^0 is placed only into high-permeability regions of the barrier, these costs could be significantly lower.

5.4.3 Nano-Scale Iron

The assumptions for arriving at cost estimates for the nano-scale iron are identical to those for micron-scale iron. The only difference is that the cost of nano-scale iron per kg of material is ranges from \$22/kg to \$44/kg. Using these values, and assuming 3 electron equivalents for each mole of iron introduced, the costs for nano-scale iron injection would be \$3.5-\$7/m^3 of water treated, \$2750-5500/kg Cr(VI) reduced, or \$275-550/(m barrier yr lifetime). The number of pore volumes treatable, and the estimated barrier lifetime are the same as for micron-scale iron because it is assumed that all of the iron is utilized in both cases. If H_2 were not utilized, these costs would be three times higher. It is possible that nano-scale iron will be fully utilized whereas micron-scale iron will not, making nano-scale iron more cost-effective than micron-scale iron. As previously noted, assuming a lower total oxidant loading, e.g. 3 mol e- equivalents/m^3 lowers these cost estimates and increase lifetimes by roughly a factor of three, and extends the barrier lifetime to ~50 years.

5.4.4 Organic Amendments

There are numerous and complex microbial reactions that take place upon injection of an organic substrate into the subsurface including respiratory and fermentative processes. During respiratory metabolism numerous potential inorganic constituents can function as electron acceptors, including O_2, NO_3^-, manganese, iron, Cr(VI), and SO_4^{-2}. For consistency and simplification, costing was based on the complete oxidation of lactate ($C_3H_6O_3$) to carbon dioxide (CO_2) with the reduction of Cr(VI), according to the following reaction stoichiometry.

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

Based on this reaction, an organic substrate can provide 4 electron equivalents per mole of carbon oxidized to CO_2, or 12 electron-equivalents/mole lactate. For Hanford groundwater, it is assumed that lactate will also be consumed to reduce DO to water, and nitrate is to N_2. It is also assumed that approximately 25% of the added carbon is incorporated into biomass production, and as above that the groundwater in the 100-D Area contains ~5.9 electron equivalents of oxidants per m^3 (Table 3.2).

Numerous organic substrates can be utilized for *in-situ* redox manipulation and the costs range from a few cents per pound (corn syrup or molasses etc.) to several dollars/lb (lactate and other proprietary compounds). For the purposes of this report we have assumed a cost of \$0.35/lb for food-grade dextrose to \$1.00/lb for a 60 wt% solution of sodium lactate. Each m^3 of solution contains on average about ~64,500 electron equivalents available to reduce oxidants in Hanford groundwater. Using a current price that ranges from \$386 to \$2,880/m^3 for 50 wt% solution of dextrose and a 60 wt% solution of sodium lactate, respectively, the cost to treat each m^3 of Hanford groundwater is estimated to range between \$0.04 to \$0.35/m^3 treated. At a Cr(VI) concentration of 1.29 mg/L, this equates to a range of \$31 to \$270/kg Cr(VI) reduced/immobilized.

6.0 SUMMARY OF RECOMMENDATIONS

6.1 Recommendations for Mending the Passive Barrier Design

The primary reasons for early breakthrough of Cr in groundwater in 17 of the ~70 ISRM barrier wells include (DOE 2004):

- Physical and chemical heterogeneity of the aquifer in the 100-D Area
- Loss of reductive capacity of the barrier in preferential flow paths
- Competing oxidants, such as NO_3^- and DO.

These aquifer characteristics persist as limitations to extending the reductive capacity of the barrier with other potential chemical or biological amendments.

With these limitations in mind, the TAT recommends two potential amendment approaches: 1) micron- or nano-scale iron delivered to preferential flow paths and 2) CaS_5 coupled with an inexpensive organic substrate applied throughout the aquifer.

Aquifer heterogeneity with significant high-permeability zones that likely are limited in reductive capacity was identified as a primary cause of premature breakthrough of Cr(VI) in the barrier. The emplacement of additional reductive mass in these high-permeability zones could significantly extend barrier performance. The addition of solid ZVI in these zones could provide a preferred solution. A prerequisite for success of this approach is accurate determination of the dominant flow paths where loss of reductive capacity is expected within the aquifer in the vicinity of the barrier and design of a system for targeted emplacement of the solid ZVI. A combination of geophysical and hydrogeochemical characterization tools, as well as conceptual and mathematical models, is discussed in the "Mending the ISRM Barrier" report (DOE, 2004) for flow delineation.

Injection of CaS_5, coupled with an inexpensive organic substrate, is expected to promote enhanced reductive capacity with longevity equal to, or perhaps greater than, the sodium dithionite. The disadvantage of this amendment combination is that the frequency of re-injection may be similar or only slightly less than that required using dithionite as a lixiviant due to the high groundwater flux and continuing source. Laboratory and field testing is required for both of these potential amendments before a mending lixiviant can be selected.

The laboratory and field-testing should be designed to collect information on the longevity and the cost of the preferred amendment. This testing can be used to quantitatively evaluate the chemical dose, method of introduction, and site-specific longevity of each amendment. Although the cost of micron- and nano-scale iron application (per cubic meter of water treated) could be twice that of CaS_5 plus organic substrate reagent (see Section 5.4), the expected longevity of the iron amendment may offset the initial cost investment. The use of CaS_5 plus organics in the passive-barrier design will require a controlled strategy of preferential and multiple injections due to the shorter-term effectiveness of the amendment in the subsurface. The issue of amendment delivery is paramount to the discussions of effectiveness and cost. CaS_5 plus organic substrate may be better applied for active remediation and ZVI may be more appropriate for mending the passive barrier. These are only hypotheses that must be tested prior to making any selections.

6.2 Recommendations for Active Treatment of the Chromium Plume

The ISRM barrier was designed and is operated as part of an interim solution to treat the Cr(VI) plume to prevent affected groundwater from reaching the Columbia River. The current passive barrier design may be unable to meet the interim and long-term objectives of mitigating long-term ecological impacts to the river system for the many reasons discussed in this report. Issues that further complicate the ability to predict passive barrier performance with confidence include uncertainties in the Cr source location(s) and aquifer heterogeneities. The later controls plume direction and flow rate, reductive capacity (i.e. ferric and ferrous iron abundance) of the native sediments, the optimum amendment selection, as well as where and how it is delivered, and its longevity. An accurate conceptual understanding of how preferential flow zones affect source and plume migration through the barrier and to the river system would provide a powerful tool to evaluate passive versus active barrier design strategies, and their relative cost benefits. The TAT recommends that a strategic effort to collect new and interpret existing data to characterize the aquifer system be undertaken.

Because a final remedy for 100-D Area groundwater treatment is expected to be in place by 2012, the TAT recommends that DOE-RL and the technical staff consider the benefits of augmenting the passive barrier with active source treatment and plume control. With this in mind, the TAT reviewed various active treatment options:

- Option 1: Source Treatment with Passive Barrier. This option involves source treatment via addition of CaS_5 with organic substrate through a grid of infiltration galleries in conjunction with ZVI introduction in preferential flow paths along the ISRM barrier. The shallow infiltration galleries would be installed and utilized to deliver chemical amendments, such as CaS_5.
- Option 2: Source Treatment with Hydraulic Control and Treatment at Barrier Wells. This option entails source treatment via CaS_5 plus organic substrate addition, as described in Option 1, in combination with recirculation of CaS_5 plus biological substrate through the upgradient and downgradient line of barrier wells to provide effective hydraulic control and treatment at the current barrier location.

- Option 3: Source Treatment with Active Plume Control. This option includes source treatment via CaS_5 plus organic substrate addition in combination with recirculation of reductant (CaS_5 + organic substrate)-bearing water in the barrier wells (Option 2). In addition, reductant-bearing water would be introduced simultaneously along the edges of the groundwater plume by either direct-push injection or infiltration galleries.

Option 3 represents the most aggressive and costly treatment approach, but is expected to be the most expedient. Options 1 and 2 are likely to be less expensive, but may require similar treatment times. The TAT recommends that Hanford personnel consider each of these three options during the preparation of the Remedial Investigation/Feasibility Study.

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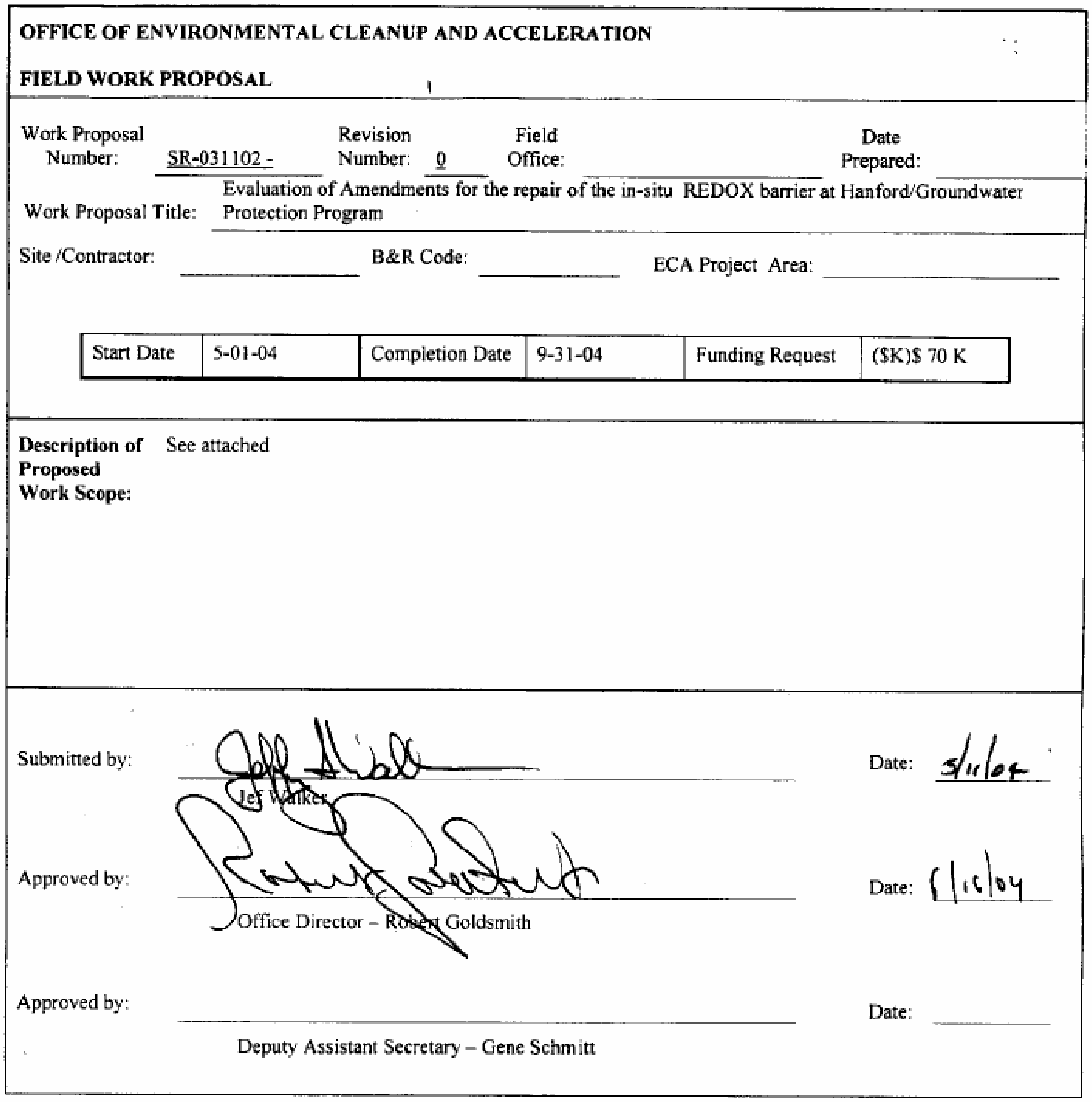
APPENDIX A TECHNICAL ASSISTANCE REQUEST



OFFICE OF ENVIRONMENTAL CLEANUP AND ACCELERATION

FIELD WORK PROPOSAL

Work Proposal Number: SR-031102 - Revision Number: 0 Field Office: Date Prepared:

Work Proposal Title: Evaluation of Amendments for the repair of the in-situ REDOX barrier at Hanford/Groundwater Protection Program

Site /Contractor: B&R Code: ECA Project Area:

Start Date	5-01-04	Completion Date	9-31-04	Funding Request	($K)$ 70 K

Description of Proposed Work Scope: See attached

Submitted by: Date: 5/11/04

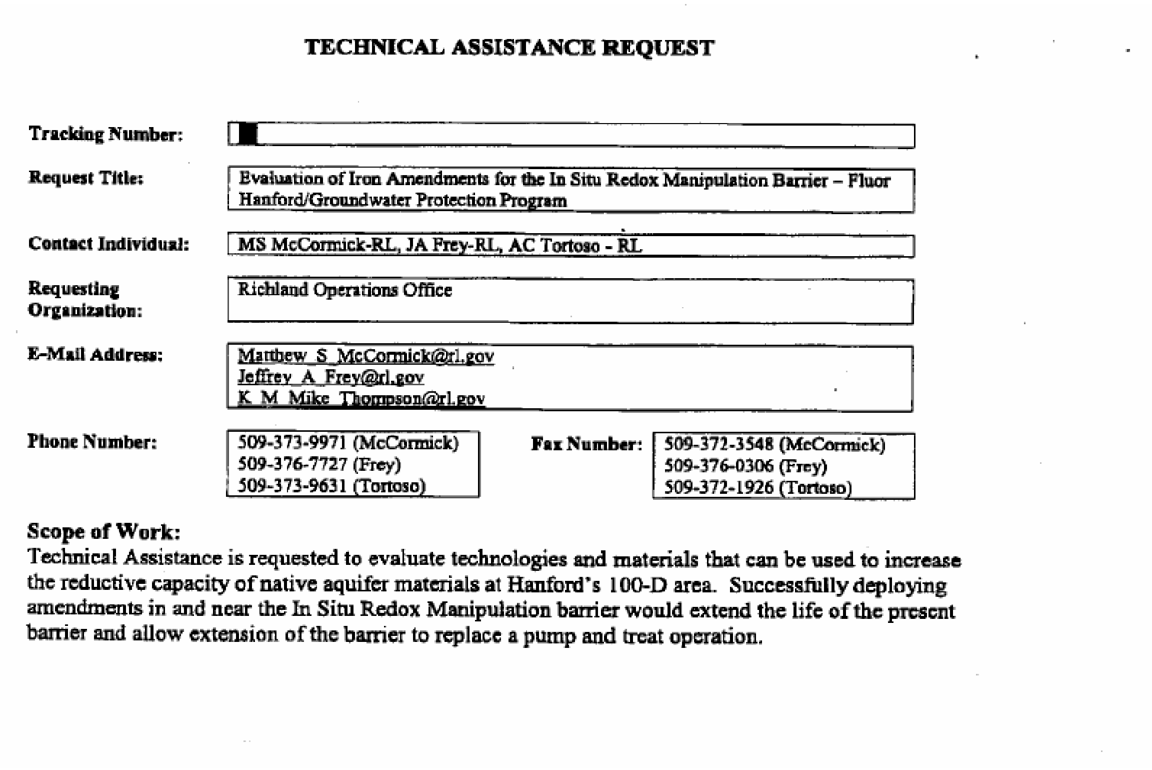
Jef Walker

Approved by: Date: 6/16/04

Office Director – Robert Goldsmith

Approved by: Date:

Deputy Assistant Secretary – Gene Schmitt



TECHNICAL ASSISTANCE REQUEST

Tracking Number:	
Request Title:	Evaluation of Iron Amendments for the In Situ Redox Manipulation Barrier – Fluor Hanford/Groundwater Protection Program
Contact Individual:	MS McCormick-RL, JA Frey-RL, AC Tortoso - RL
Requesting Organization:	Richland Operations Office
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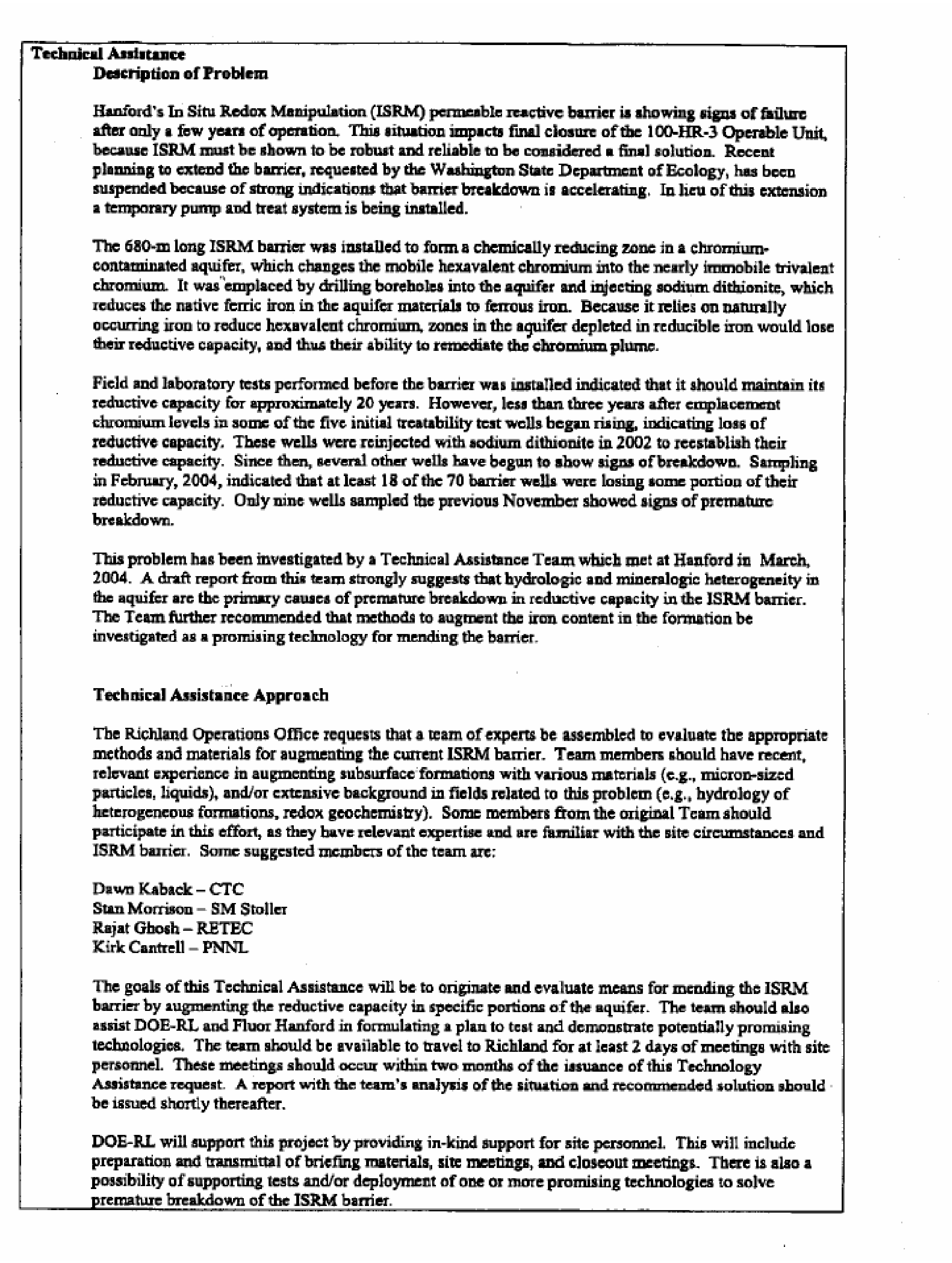
Phone Number:	509-373-9971 (McCormick) 509-376-7727 (Frey) 509-373-9631 (Tortoso)	**Fax Number:**	509-372-3548 (McCormick) 509-376-0306 (Frey) 509-372-1926 (Tortoso)

Scope of Work:

Technical Assistance is requested to evaluate technologies and materials that can be used to increase the reductive capacity of native aquifer materials at Hanford's 100-D area. Successfully deploying amendments in and near the In Situ Redox Manipulation barrier would extend the life of the present barrier and allow extension of the barrier to replace a pump and treat operation.



Technical Assistance

Description of Problem

Hanford's In Situ Redox Manipulation (ISRM) permeable reactive barrier is showing signs of failure after only a few years of operation. This situation impacts final closure of the 100-HR-3 Operable Unit, because ISRM must be shown to be robust and reliable to be considered a final solution. Recent planning to extend the barrier, requested by the Washington State Department of Ecology, has been suspended because of strong indications that barrier breakdown is accelerating. In lieu of this extension a temporary pump and treat system is being installed.

The 680-m long ISRM barrier was installed to form a chemically reducing zone in a chromium-contaminated aquifer, which changes the mobile hexavalent chromium into the nearly immobile trivalent chromium. It was emplaced by drilling boreholes into the aquifer and injecting sodium dithionite, which reduces the native ferric iron in the aquifer materials to ferrous iron. Because it relies on naturally occurring iron to reduce hexavalent chromium, zones in the aquifer depleted in reducible iron would lose their reductive capacity, and thus their ability to remediate the chromium plume.

Field and laboratory tests performed before the barrier was installed indicated that it should maintain its reductive capacity for approximately 20 years. However, less than three years after emplacement chromium levels in some of the five initial treatability test wells began rising, indicating loss of reductive capacity. These wells were reinjected with sodium dithionite in 2002 to reestablish their reductive capacity. Since then, several other wells have begun to show signs of breakdown. Sampling in February, 2004, indicated that at least 18 of the 70 barrier wells were losing some portion of their reductive capacity. Only nine wells sampled the previous November showed signs of premature breakdown.

This problem has been investigated by a Technical Assistance Team which met at Hanford in March, 2004. A draft report from this team strongly suggests that hydrologic and mineralogic heterogeneity in the aquifer are the primary causes of premature breakdown in reductive capacity in the ISRM barrier. The Team further recommended that methods to augment the iron content in the formation be investigated as a promising technology for mending the barrier.

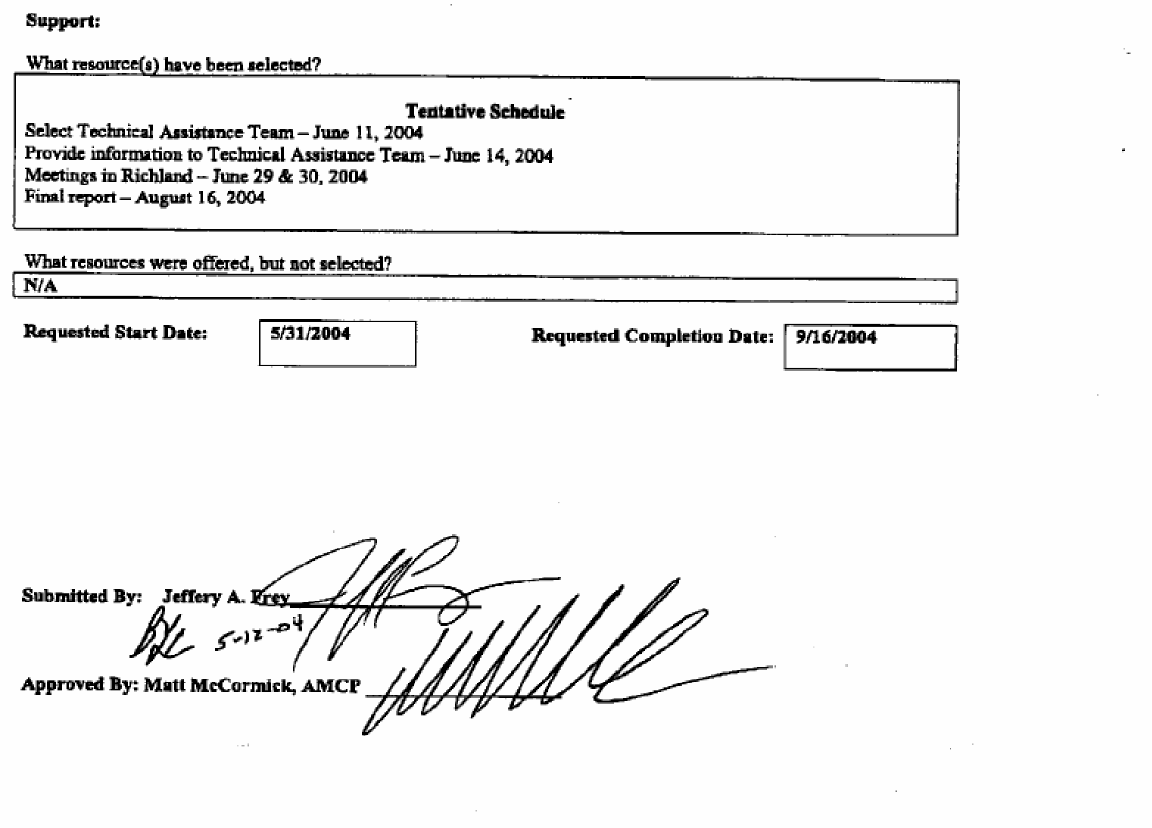
Technical Assistance Approach

The Richland Operations Office requests that a team of experts be assembled to evaluate the appropriate methods and materials for augmenting the current ISRM barrier. Team members should have recent, relevant experience in augmenting subsurface formations with various materials (e.g., micron-sized particles, liquids), and/or extensive background in fields related to this problem (e.g., hydrology of heterogeneous formations, redox geochemistry). Some members from the original Team should participate in this effort, as they have relevant expertise and are familiar with the site circumstances and ISRM barrier. Some suggested members of the team are:

Dawn Kaback – CTC
Stan Morrison – SM Stoller
Rajat Ghosh – RETEC
Kirk Cantrell – PNNL

The goals of this Technical Assistance will be to originate and evaluate means for mending the ISRM barrier by augmenting the reductive capacity in specific portions of the aquifer. The team should also assist DOE-RL and Fluor Hanford in formulating a plan to test and demonstrate potentially promising technologies. The team should be available to travel to Richland for at least 2 days of meetings with site personnel. These meetings should occur within two months of the issuance of this Technology Assistance request. A report with the team's analysis of the situation and recommended solution should be issued shortly thereafter.

DOE-RL will support this project by providing in-kind support for site personnel. This will include preparation and transmittal of briefing materials, site meetings, and closeout meetings. There is also a possibility of supporting tests and/or deployment of one or more promising technologies to solve premature breakdown of the ISRM barrier.



Support:

What resource(s) have been selected?

Tentative Schedule

Select Technical Assistance Team – June 11, 2004
Provide information to Technical Assistance Team – June 14, 2004
Meetings in Richland – June 29 & 30, 2004
Final report – August 16, 2004

What resources were offered, but not selected?

N/A

Requested Start Date: 5/31/2004

Requested Completion Date: 9/16/2004

Submitted By: Jeffery A. Frey

5-12-04

Approved By: Matt McCormick, AMCP

APPENDIX B WORKSHOP ATTENDEES

Technical Assistance Workshop

NAME	COMPANY	PHONE	e-MAIL
Jim Szecsody	PNNL	509-372-6080	jim.szecsody@pnl.gov
Vince Vermeul	PNNL	509-376-8316	vince.vermeul@pnl.gov
John Fruchter	PNNL	509-376-3937	john.fruchter@pnl.gov
Beth Moore, TAT	DOE-HQ	202-586-6334	Beth.moore@em.doe.gov
Dib Goswami	Ecology	509-735-3015	Dgos461@ECY.WA.gov
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Bruce Wielinga, TAT	MFG, Inc.	970-223-9600	bruce.wielinga@mfgenv.com
Greg Lowry, TAT	CMU	412-268-2948	glowry@cmu.edu
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Jim V. Rouse, TAT	MWH	303-526-5493	Jim.rouse@mwhglobal.com
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Dawn Kaback, TAT	*CTC*	303-297-0180 ext. 111	kabackd@ctc.com
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Arlene Tortoso	DOE-RL	509-373-9631	Arlene_C_Tortoso@rl.gov

APPENDIX C TECHNICAL ASSISTANCE WORKSHOP AGENDA

AGENDA
Evaluation of Chemical Amendments For Mending In Situ Redox Manipulation Barrier Technical Assistance Workshop

Room 1-C1, 1200 Jadwin Avenue
Richland WA
July 26-29, 2004

Monday, July 26

1:30-5:00	Site Tour (ISRM at 100 D)	V. Vermuel, J. Szecsody All Team Members

Tuesday, July 27

8:30-8:45	Welcome and Introductions	A. Tortoso and S. Petersen
8:45-9:00	Regulatory Update	A. Tortoso
9:00-9:30	Background – ISRM Concept and Design	J. Fruchter
9:30-9:45	Current Status of ISRM Barrier	S. Petersen
9:45-10:15	Review ISRM TAT Report	D. Kaback, R. Ghosh, Wielinga
10:15-10:30	BREAK	
10:30-10:45	Workshop Objectives	S. Petersen and R. Ghosh
10:45-11:20	Barrier Longevity, Redox Reactivity	J. Szecsody
11:20-12:00	Characterization of Formation Heterogeneities	V. Vermeul
11:45-1:00	LUNCH	
1:00-5:00	Discussions/Questions w PNNL, Fluor. DOE, and State Personnel Team Discussions and Brain Storming Solutions (possibly more discussions with members of Hanford Project Team, if needed, TBD)	All

Wednesday, July 28

8:30-12:00	Evaluation of Options/Recommendations	Team
12:00-1:00	LUNCH	
1:00-2:00	Discussion/Questions w Fluor & PNNL	All
2:00-4:00	Finalization of Recommendations	Team
4:00-5:00	Preparation of Out briefing	Team

Thursday, July 29

8:30-9:30	Complete Out briefing Package	Team
9:30-10:30	Out-briefing/Discussion w DOE and Fluor	All

APPENDIX D PROCEDURE TO ESTIMATE LIFETIME OF VARIOUS AMENDMENTS

PROCEDURE TO ESTIMATE LIFETIME OF VARIOUS AMENDMENTS

The basic concept of the ISRM barrier is to have a zone with sufficient reductant so that the Cr(VI) in the groundwater passing through the barrier will be reduced to Cr(III) and subsequently precipitated as an oxyhydroxide within the aquifer. The reductants within the barrier will either be derived from materials originally in the aquifer that were reduced by the lixiviant or reductants directly added into the aquifer. The characterization of the site and the design of the barrier will depend on the goals for the barrier.

It must be established that there is sufficient reductant in the barrier to reduce the Cr(VI) in the groundwater passing through the barrier in the time period of interest. The number of electron equivalents of reductants in the barrier, M_R, can be estimated by integrating the reduction capacity of the barrier, S_R, in equivalents per kilogram of soil, over the volume of the barrier (m^3), according to the following equation:

$$\boxed{M_R = \iiint_V S_R(x,y,z)(1-\theta_s)\,\rho_b\,dxdydz} \quad (1)$$

where θ_s is the porosity of the aquifer, ρ_b is the dry bulk density, and V denotes that the integration is over the volume of the barrier. If the barrier is to be the final remedy, then information about the source must be obtained to assess its lifetime and the total number of equivalents of oxidants that can consume the reductant capacity of the barrier. This information would include the number of equivalents of Cr(VI), the concentration of Cr(VI) in the groundwater passing through the source area, most importantly, the concentrations of other oxidants (e.g. DO and NO_3^-) as these represent a significant portion of the oxidants in the groundwater. It should be reasonably demonstrated that $M_R > M_{ox}$ where M_{ox} is the number of equivalents of oxidants entering the barrier over the lifetime of the Cr(VI) source.

If the barrier is considered to be an interim remedy over some required interval of time, Δt_{req} (days), then it should be demonstrated that there is sufficient equivalents of reductant to reduce all of the oxidants, including the target contaminant, that are transported to the barrier over that time interval. The required mass of reductant in equivalents must then meet the following constraint:

$$\boxed{M_R \geq 1000\,\Delta t_{req}\,q_{gw}\,C_{ox}\,A} \quad (2)$$

where q_{gw} is the specific discharge of groundwater (m/day), C_{ox} is the concentration in equivalents per liter of groundwater, and A is the cross-sectional area normal to the direction of groundwater flow (m^2).

Another key factor in the application of PRBs such as the ISRM is the rate of Cr(VI) reduction relative to the rate of advective transport through the barrier. The time for the reduction reaction to decease the concentration from its initial value, C_0, to the MCL, C_{MCL} (22 μg/L), should be less than the residence time of the contaminated groundwater in the reactive barrier. For example, if the rate of reduction of Cr(VI) follows a first-order rate equation with an apparent pseudo-first-order rate coefficient, k,

$$\boxed{\frac{dC}{dt} = -kC} \tag{3}$$

the time for the concentration of Cr(VI) to decrease from C_0 to C_{MCL} must be less than the residence time of the contaminated parcel of water within the aquifer

$$\boxed{\frac{\ln\left(C_o / C_{MCL}\,)\right)}{k} \le \frac{x_B}{v_w}} \tag{4}$$

where x_B is the width of the reactive barrier and v_w is the groundwater velocity. The apparent rate coefficient will depend on the mass of amendment per unit volume of barrier, and may decrease over time as the amendment ages. The difficulty in applying this criterion to the ISRM arises in applying the appropriate rate equation and obtaining the pertinent rate coefficients.

In principle, the estimation of the time to breakthrough of the Cr(VI) can be made by solving for Δt in Eq. (2). However, it should be emphasized that when applying any of these equations the system is both hydraulically and chemically heterogeneous. The concentration of Cr(VI) in the downgradient wells will likely exceed the MCL long before any lifetime calculated using average material properties.

The average concentration in a monitoring well, $\overline{C}$, that is pumped to obtain the sample is given by

$$\boxed{\overline{C} = \frac{1}{B}\int_0^B \left(\frac{K(z)}{\overline{K}}\right) C(z)\,dz} \tag{5}$$

where K(z) and C(z) are the spatially dependent is the hydraulic conductivity and concentration, respectively, and B is the saturated thickness of the aquifer. Eq. (5) can be written in discrete form as

$$\boxed{\overline{C} = \sum_i \left(\frac{K_i}{\overline{K}}\right)\left(\frac{b_i}{B}\right) C_i} \tag{6}$$

where K_i, C_i, and b_i are the hydraulic conductivity, concentration, and thickness of the discrete flow paths intercepted by the well. One simple approach for improved estimates of barrier lifetime is to

1. Estimate the number of standard deviations in ln K before $\overline{C} \ge C_{MCL}$ using Eq. (6) with the assumption of a log-normal distribution in K, using an estimate of the

autocorrelation length scale for b_i., and the maximum measured Cr(VI) concentration in the zones with $\ln K \geq \ln \overline{K} + n\sigma_{\ln K}$ and zero concentration for all zones with $\ln K \leq \ln \overline{K} + n\sigma_{\ln K}$

2. Develop an empirical relationship between S_R and K.
3. Calculate S_R at the K value where $\overline{C} \geq C_{MCL}$
4. Calculate the lifetime based on Eq. (2) using the estimate of S_R, the K value where breakthrough occurs.

It is recommended that this type of procedure be applied to estimate the lifetime of various amendments when sufficient aquifer characterization data, and laboratory treatability data are available.