WSRC-STI-2006-00347

Supplemental Columbia River Protection Activities at the Department of Energy Hanford Site: 2006 Technical Peer Review

Prepared for
Department of Energy Office of Clean-up Technology, EM-21
Washington, D.C.

December 2006

Washington Savannah River Company Savannah River Site Aiken, SC 29808 **Prepared for the U.S. Department of Energy Under Contract Number DEAC09-96-SR18500**	SRNL™ SAVANNAH RIVER NATIONAL LABORATORY

Cover Photo: Oblique view overhead photograph of the 100 N Area adjacent to the Columbia River at the Department of Energy Hanford Reservation in Washington State

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Prepared For
U.S. Department of Energy

Supplemental Columbia River Protection Activities at the Department of Energy Hanford Site: 2006 Technical Peer Review

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SUPPLEMENTAL COLUMBIA RIVER PROTECTION ACTIVITIES AT THE DEPARTMENT OF ENERGY HANFORD SITE: 2006 TECHNICAL PEER REVIEW

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I. EXECUTIVE SUMMARY

Prompted by a $10 million Congressional allocation to identify supplemental actions to protect the Columbia River from groundwater contamination beneath the Hanford Reservation, the U. S. Department of Energy (DOE) Environmental Management (EM) Office of Clean-up Technology identified twenty-three potential technical projects and then down-selected ten of these for further evaluation. An independent expert peer review was conducted for the ten down-selected proposals. The review panel consisted of twenty-three recognized subject matter experts that broadly represented academia, industry, and federal laboratories. Of the initial ten proposals reviewed, one was given unconditional support, six were given conditional support, and three were not supported as proposed. Three additional proposals were then submitted by DOE for review – these proposals were structured, in part, to respond to the initial round of technical peer review comments. Peer reviews of these additional proposals provided conditional support. For those proposals that received conditional support, DOE requested specific implementation and work plans and assessed whether the plans adequately addressed the technical conditions identified by the review panel. The final list of technology proposals receiving support, or conditional support, primarily focused on understanding and reducing the potential impacts of uranium, chromium, and strontium from facilities adjacent to the Columbia River, with a secondary focus on understanding and limiting the future Columbia River impacts from the large carbon tetrachloride groundwater plume underlying and downgradient of the Hanford Central Plateau facilities. The results and recommendations of the peer reviews informed the final DOE project selections and supported implementation of the selected projects to protect the Columbia River and address groundwater contamination at Hanford.

II. INTRODUCTION AND BACKGROUND

In November 2005, Congress allocated $10 million in targeted funding to supplement actions to protect the Columbia River from contaminants migrating in the groundwater beneath the DOE Hanford Reservation in Washington State. The $10 million Congressional allocation and mandate is supported by the following two technical goals:

1. Improve DOE efforts to protect the Columbia River from contaminants migrating from the Hanford Site.
2. Provide new or supplementary technology, where needed, to identify and solve contaminant migration issues.

According to the House Senate Conference Committee: "... The conferees are concerned about DOE's efforts to protect contaminants from reaching the Columbia River. <u>Technology used in several remedies is not performing satisfactorily, and there is a lack of new technologies to address contamination issues.</u>" They noted -- the problem impeding site closure is poor performance of existing remedies (e.g., pump and treat systems for chromium and uranium, ^{90}Sr leaching into the river above guidelines, etc.) Many of these remedies were implemented using "records of decision" (RODs) that are currently undergoing review – the supplemental funding provides an opportunity to address known poor performance in a proactive manner and to increase DOE credibility with regulators stakeholders and governments.

This supplemental technology program is a major initiative for DOE -- successful implementation is important to Congress, regulators, stakeholders, and tribal and local governments. Independent and broad based peer review by recognized national experts is critical, supporting DOE management and decision-making, as well as documentation and performance metrics. DOE EM is administering the supplemental funding in collaboration with DOE Richland (RL). The Savannah River National Laboratory (SRNL) coordinated the independent technical peer reviews for DOE EM.

Proposed Supplemental Technology Projects

The DOE EM Office of Clean-up Technology identified twenty-three potential technical projects and then down-selected ten of these for further evaluation. This portfolio of ten potential projects was identified based on the general criteria of "relevance," "risk reduction," "baseline improvement," "implementability" and "acceptability." Preliminary recommendations from the peer reviews of the initial ten proposals resulted in the submission of three new or revised proposals for review. The resulting proposed portfolio represents a balance of these factors and specifically targets underperforming remediation technologies that address the following contaminants (and areas) at Hanford:

- Chromium (Cr(VI)) in 100-D & 100-K Areas
- Strontium (^{90}Sr) in the 100-N Area
- Uranium (U) in the 300 Area
- Carbon tetrachloride (CCl_4) in the 200 Areas
- Technetium in the deep vadose zone in the 200 Areas

The DOE-identified supplemental technology proposals associated with each contaminant of concern appear in the table below.

Contaminant	Supplemental Technology Proposals
Strontium (^{90}Sr)	▪ Sequestration of ^{90}Sr Subsurface Contamination in the Hanford 100-N Area by Surface Infiltration of an Apatite Solution ▪ Phytoremediation – Treatability Study along the 100-N Riparian Zone
Chromium (Cr(VI))	▪ Refine Location of the Chromium Source at the 100-D Area ▪ Chromium Vadose Zone Characterization and Geochemistry *(additional proposal)* ▪ Refine Location of the Chromium Source at the 100-D Area and Support a Geochemical/Mineralogical Study of Chromium in the Vadose Zone *(additional proposal)* ▪ Initial Calcium Polysulfide Test for Accelerated Clean Up of the Southwestern Chromium Plume in the 100-D Area ▪ Hanford 100-D Area Treatability Demonstration: Accelerated Bioremediation through Polylactate Injection Field Test *(additional proposal)* ▪ Electrocoagulation for Accelerated Clean Up of the Northeastern Chromium Plume in the 100-D Area Inject Micron-sized Iron into the Deteriorating Portions of the ISRM Barrier
Uranium (U)	▪ 300 Area Uranium Plume Treatability Demonstration Project: Uranium Stabilization through Polyphosphate Injection
Carbon tetrachloride (CCl_4)	▪ Carbon Tetrachloride and Chloroform Attenuation Parameter Studies: Heterogeneous Hydrolytic Reactions ▪ Deep Carbon Tetrachloride (CT) Contaminant Assessment in the Vicinity of 216-Z-9
Technetium (^{99}Tc)	▪ Insitu Reactive Nanoporous Metal Phosphate Barrier for Sequestration of Technetium (VII)

A technical peer review of the proposals was convened to help identify issues and uncertainties that will be used by DOE to finalize and/or modify their selections and plans.

III. PEER REVIEW APPROACH

Peer Review Objectives

The primary objective of the peer reviews was to evaluate the proposed supplemental technology(ies) in the context of the target contaminant plume. The reviews considered the technical basis of the proposal, the proposed implementation strategy, the proposed performance metrics, etc. In the course of the review, the participants evaluated the underpinning science, the cost and level of effort, potential alternatives, etc. Some of the proposed activities are the result of previous broad based scientific peer review/recommendation panels. The peer review approach involved looking over these previous panel reports, which required reviewing additional background material, but expedited the overall process since the reviewers could build on the earlier comments and recommendations and provide a rapid assessment of the implementation.

The peer reviews focused on evaluating the proposals in terms of achieving the Congressional Conference Committee mandate -- To supplement and improve *"DOE's efforts to protect contaminants from reaching the Columbia River,"* including a supplemental activity's ability to:

- Provide new or supplemental technology approaches, where appropriate, to identify and solve contaminant migration issues;
- Provide integrated (not fragmented) solutions to contaminant migration issues;
- Be consistent with previous recommendations and reviews when available;
- Directly and adequately address selection criteria: relevancy, risk reduction, baseline improvement, implementability, acceptability.

The peer review objectives also recognized a few key related items/constraints:

- No Congressional mandate for a general program of testing for new environmental technologies – only those that address the scope;
- No strict requirement to only use new technologies – only a mandate to introduce new technology where current systems are not performing satisfactorily.

Peer Review Process

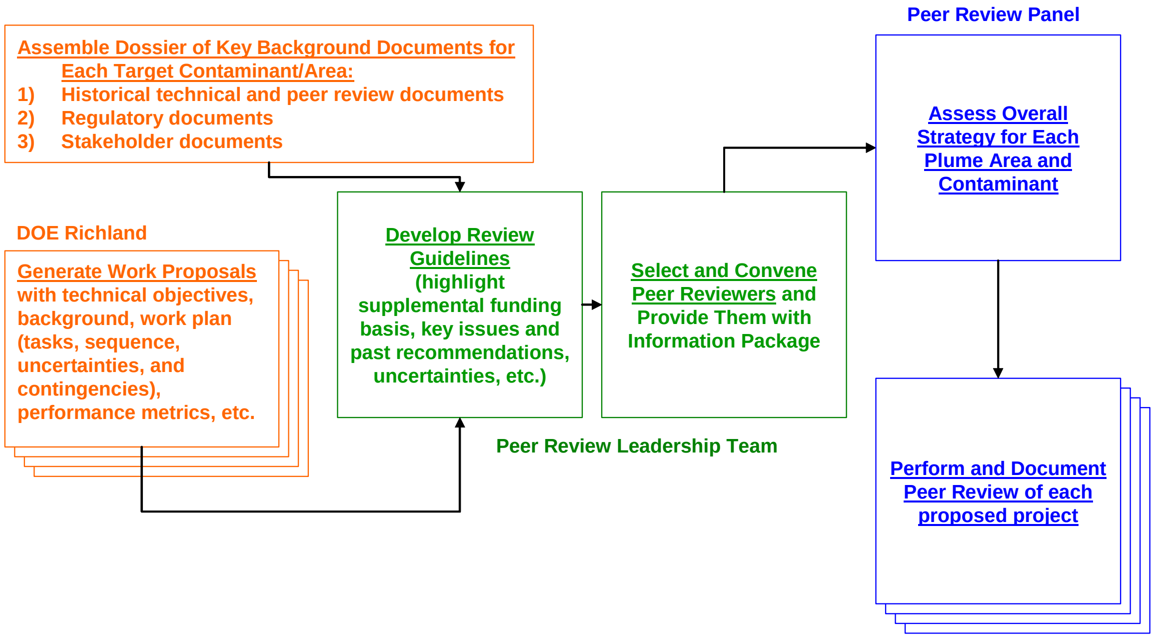
All of the proposed supplemental technologies and actions identified by DOE were assessed by a broad-based and independent peer review. Activities that have already been vetted through independent broad-based peer review proceeded using an expedited peer review process, while the remainder of the portfolio underwent a more detailed "full" peer review process. A full peer review was also required where significant unresolved technical issues were identified by the Steering Committee (e.g., the ability of geophysics to identify chromium sources at low concentrations, or the viability of nanoparticle sorption of Tc in the vadose zone) or for projects where there are specific technical risks (e.g., phytoextraction of strontium and the potential for contaminated plants to leave the site). Peer reviewers documented their findings and comments on a review template developed to promote consistency.

The peer reviews were conducted at a level of detail that is slightly more than a careful review of a journal article. The reviews were performed in four batches. The first batch addressed contaminants that are currently documented to be entering the Columbia River. This batch included the target plumes for three sites that are located adjacent to the River and the following contaminants – ^{90}Sr, U and Cr(VI). Reviews of this batch were completed and discussed in a peer review meeting in Salt Lake City during the last full week of March 2006. Batch two consisted of the proposal related to ^{99}Tc in the vadose zone was evaluated and discussed in a peer review meeting in Nashville on April 24, 2006. The third batch included the two proposals related to CCl_4, which were reviewed and discussed via conference call on May 9, 2006. In addition, recommendations from the initial peer reviews resulted in three revised proposals, which were subsequently peer reviewed as a fourth and final batch.

For each proposal, the peer reviewers:

- Considered background information prepared by DOE-RL for each target plume area and contaminant (previous reviews and recommendations, key information, regulatory commitments, etc.)
- Assessed the overall logic and completeness of meeting the goal of protecting the Columbia River (these assessments will include both baseline and supplemental activities)
- Evaluated the individual technical proposals to be performed within the plume

The sequence is shown in graphical form below:



IV. PEER REVIEW RESULTS

Each peer review includes a summary of findings and comments from the peer reviewers, which indicates whether the proposal received:

- Support – Peer reviewers agreed with the science, technical approach, implementation, and performance metrics described in the proposal,

- Conditional support – Peer reviewers agreed with the general premise of the proposal, but had some issues with the technical approach, implementation, or performance metrics described in the proposal. The peer reviews recommended DOE consider funding these proposals, assuming the authors take the steps necessary to address the issues and comments developed by the peer reviews, or,

- No support – Peer reviewers disagreed with the science used in the proposal or had substantial concerns about the technical approach, implementation, or performance metrics. The peer reviews recommended DOE not fund these proposals as written.

Of the initial ten proposals, one was given unconditional support, six were given conditional support, and three were not supported as proposed. Three additional proposals were submitted for review in response to initial round of technical peer review comments. These proposals were structured, in part, to address the recommendations on two of the previously unsupported proposals. Peer reviews of these additional proposals provided conditional support. For those proposals that received conditional support, DOE requested specific implementation and work plans and assessed whether these plans adequately addressed the technical conditions identified in the peer review. The following table provides the titles of the proposals (organized by contaminant of concern), a brief peer review summary, and the peer review results.

Contaminant	Proposal	Summary	Peer review results
Strontium (^{90}Sr)	Sequestration of ^{90}Sr Subsurface Contamination in the Hanford 100-N Area by Surface Infiltration of an Apatite Solution	The panel provides conditional support for the infiltration of an apatite-forming solution to sequester ^{90}Sr. The panel supports the systematic, "defense in depth" approach to sequestering ^{90}Sr, which combines current plans for injection of apatite solution (calcium-citrate-phosphate) with the infiltration of apatite solution, possible phytoremediation, and natural attenuation. However, some specific technical and implementation issues should be addressed, including more thorough demonstration of how the proposed project benefits are more appropriate than other alternatives and discussion of the possible design constraints and variations in reagent chemistry to minimize collateral environmental impacts. The panel also recommends identifying a hydrologist, geologist or engineer to serve as a substantive collaborator on this project.	conditional support
	Phytoremediation – Treatability Study along the 100-N Riparian Zone	The panel supports the proposal with some qualifications that need to be addressed. Specific issues identified by the panel relate to the sequencing of technologies, identifying performance metrics, performing tests to better understand potential collateral impacts of the phytoremediation system (e.g., potential ecosystem exposures and releases), and ensuring estimated lifecycle costs are realistic.	conditional support
Chromium (Cr(VI))	Refine Location of the Chromium Source at the 100-D Area	The panel supports the goal of refining the source location of chromium contamination in the Hanford 100-D Area as part of the overall systems approach; however, the panel does not recommend funding the proposal as written and recommends a new proposal be written to replace this one. The panel does not believe surface geophysics can be used to directly identify the source, but likely has a significant role in furthering understanding of the hydrogeology in the source area. The panel recommends a two-pronged approach for the problem: 1) investigate a Cr source known to exist at the 100-B Area and possibly other sources that may be identified during excavation of piping in the 100-D Area in	no support

		2006 to enhance understanding of Cr transport, fate, and form in the vadose zone by using geophysical and geochemical methods (possibly using Enhanced Access Penetration System [EAPS] or other direct push technology to install boreholes); 2) if source identification is successful in the 100-B Area, utilize similar methods in the 100-D Area, near suspected sources.	
	(additional proposal) Chromium Vadose Zone Characterization and Geochemistry	The proposal addresses a valid technical need to supplement and support a systematic approach to addressing Cr(VI) at the 100D Area of Hanford. The review panel felt that this proposal, in combination with the supporting Fluor field campaign, is a significant improvement compared to the earlier proposed source identification strategy that relied primarily on geophysics. DOE should consider funding this effort – we recommend that the proposers consider the technical comments and recommendations as they finalize the work plan and schedule.	conditional support
	(additional proposal) Refine Location of the Chromium Source at the 100-D Area and Support a Geochemical/Mineralogical Study of Chromium in the Vadose Zone	The proposal addresses a valid technical need for source location delineation as an important part of a systematic approach to addressing Cr(VI) at the 100D Area of Hanford. The review panel felt that this proposal, in combination with the supporting geochemistry study, is a significant improvement compared to the earlier proposed source identification strategy that relied primarily on geophysics. DOE should consider funding this effort, incorporating the peer review's technical comments and recommendations in the work plan and schedule.	conditional support

	Inject Micron-sized Iron into the Deteriorating Portions of the ISRM Barrier	The panel supports the project, but provides specific recommendations for designing a more detailed workplan that addresses issues and uncertainties documented below. Primary issues and uncertainties relate to delivery of zero valent iron (ZVI), presence of co-contaminants and byproduct generation, and longevity. Establishment of specific project objectives and metrics to measure performance must be developed. The panel believes the project fits well as part of the systems approach to reduce chromium contamination reaching the Columbia River. The fact that this project builds upon the existing infrastructure of the ISRM is beneficial. Re-scope the laboratory work to answer questions related to issues and uncertainties and then rapidly demonstrate it in the field to test proof-of-principle.	conditional support
	Field Test Electrocoagulation for Accelerated Clean Up of the Northeastern Chromium Plume in the 100-D Area	The panel generally supports performing the electrocoagulation (EC) field test to determine the ability of EC to optimize the existing pump and treat system to accelerate the reduction of the Cr(VI) contaminant plume in the Hanford 100-D Area. However, the panel identified several specific technical and implementation components of the EC system that need to be carefully addressed, identified, or evaluated. Also, other viable alternative technologies should be screened to confirm/assure the selection of EC. The panel expressed concern over the requested funding and provided input on strategies to maximize value.	conditional support
	Initial Calcium Polysulfide Test for Accelerated Clean Up of the Southwestern Chromium Plume in the 100-D Area	The panel does not support the proposal as written; however, the panel does support the concept of upgradient treatment to augment the performance of the ISRM barrier. Although calcium polysulfide (CPS) will effectively reduce upgradient Cr(VI) contamination to Cr(III), the panel believes there are alternatives that are likely to be better suited to the upgradient (of the ISRM barrier) treatment of the Cr plume. These alternatives should be evaluated, in terms of costs and ease of implementation and longevity, to determine their relative effectiveness in comparison to CPS.	no support

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<td>(additional proposal)
Hanford 100-D Area Treatability Demonstration: Accelerated Bioremediation through Polylactate Injection</td>
<td>The review panel believes this is a significantly improved proposal compared to the earlier proposed calcium polysulfide treatment. The proposed approach is an appropriate part of a “defense in depth” concept for immobilizing chromium in the subsurface before it reaches the Columbia River. The proposed action is upgradient of the “to be repaired” ISRM barrier and downgradient of the suspected source areas (for which various ideas for locating and removing/treating are also proposed). The proposed project will produce reducing conditions and reduce dissolved oxygen, nitrate and Cr(VI) levels in the groundwater, thus extending the service life of the ISRM. DOE should consider funding with the following caveats considered and addressed in developing the final work plan:

Perform a more complete evaluation of alternatives and adjust the proposal as needed (e.g., justify the selected electron donor and well configuration).
Reduce the Lab and theoretical components of the work and target a total cost of approximately $1000K. The reviewers felt that the initial effort should be a proof-of-principle test, quickly applied in the field, to determine if a low-cost nutrient delivery system can maintain reducing conditions over reasonable time periods to enable a full-scale deployment.
Develop technically based performance criteria that focus the objective of this effort and cost effectively monitor the action in combination with the other chromium response actions that are occurring upgradient and downgradient.
</td>
<td>conditional support</td>
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Uranium (U)	300 Area Uranium Plume Treatability Demonstration Project: Uranium Stabilization through Polyphosphate Injection	The panel generally supports the proposal with some recommendations to address uncertainties. Identified issues and concerns are related to the method of injection and influence of subsurface heterogeneity, longevity of the polyphosphate apatite barrier, approaches to laboratory experiments, geochemical impacts resulting from the injection, and long-term monitoring of the uranium plume. The proposal includes a combination of laboratory and field investigations that should provide the data required to evaluate the likelihood of successful deployment.	conditional support
Carbon tetrachloride (CCl_4)	Carbon Tetrachloride and Chloroform Attenuation Parameter Studies: Heterogeneous Hydrolytic Reactions	The panel supports the proposed study and believes it is based on appropriate and valid science to address the CT plume. Moreover, the study would fill an existing science gap at Hanford and complements and leverages the current homogenous hydrolysis study. For a large plume like CT at Hanford, hydrolysis and similar degradation processes that are traditionally neglected may be significant in limiting contaminant migration. The current remediation technology is soil vapor extraction and limited groundwater pump and treat. The proposed research is a key step in developing an overarching and long-term plan for CT and related contaminants at Hanford. Some technical issues/recommendations were identified by the panel, which should be considered by the investigators and DOE as the research plan is finalized and the work implemented. These concerns were primarily associated with the type(s) of solids used in the heterogeneous studies, the timing and sensitivity of the analysis, the total length of time needed for the study, the QA and equivalency requirements associated with a multi year study, etc.	support

	Deep Carbon Tetrachloride (CT) Contaminant Assessment in the Vicinity of 216-Z-9	The panel believes the proposal provides a creative approach for using existing infrastructure and a proven technology, aquifer testing, to assess CT contamination as dense non-aqueous phase liquid (DNAPL) in the unconfined aquifer beneath a known source zone, the 216-Z-9 Trench in the 200 West Area of the Hanford site. However, the panel does not believe sufficient detailed work has been demonstrated on the conceptual model of DNAPL potentially trapped in the unconfined aquifer and on the three-dimensional flow field to be induced during the pumping test. The panel recommends the project be conducted through two phases with a go/no go decision made after completion of Phase One. Phase One consists of three activities: 1) demonstration of the location of a potential DNAPL trap through validation of the conceptual model with surface or cross-borehole geophysics (new or existing data); 2) additional numerical modeling to determine the viability of the test to attain the objective of demonstrating the presence or absence of DNAPL based upon the location of a potential DNAPL trap, selection of a pumping well, and design of the pumping test; and 3) evaluation of three confidence intervals related to the measured CT concentration in terms of possibility of DNAPL presence or absence. Phase Two will consist of the actual pumping test. The panel recommends conducting the pumping test only if the Phase I work shows an ability to reduce uncertainty so that the proposed test could meet its objectives.	conditional support {note this work not implemented as part of final supplemental funding portfolio because proposed work plan did not meet conditions identified in the peer review}

Technetium (^{99}Tc)	Insitu Reactive Nanoporous Metal Phosphate Barrier for Sequestration of Technetium (VII)	The panel recognizes that use of a metal phosphate barrier represents an interesting and potentially promising approach for sequestration of technetium (VII) (^{99}Tc) and other select metals. While the proposal appears to address the spirit of two of the congressionally-mandated technical goals – (i) improve DOE efforts to protect the Columbia River from contaminants migrating from the Hanford Site; and (ii) provide new or supplementary technology – the panel believes that the technology described in this proposal is insufficiently developed to meet the timeline noted in the congressional mandate. As such, the panel does not recommend funding. The panel recommends that the DOE field office (Richland Operations Office) consider implementing the sequenced recommendations from the previous peer review of vadose zone technologies to treat ^{99}Tc (edited by Peterson and Fogwell, 2005). Although financial support is not recommended, the panel believes the assembled team of scientists presents a reasonably strong case to further explore the development of metal phosphate materials as a potential tool in the adsorption of technetium (VII) and other metals. It is in this light that the panel further explored specific areas of concern and made suggestions for improvement.	no support

The complete peer reviews of each supplemental technology proposal appear as appendices to this report. Issues and comments from individual peer reviewers were incorporated into a "Summary Peer Review" for each proposal. This summary is the first item in each appendix. The complete set of individual peer reviews are appended to summary peer review reports for each proposal. Peer reviews participants are listed in the beginning of each peer review report, however, to enable peer review participants to objectively review the proposals, individual comments and reviews are referred to arbitrarily by numbers rather than names.

V. PEER REVIEW PANEL

The review panel consisted of twenty-three recognized subject matter experts that represented academia, industry, and federal laboratories. The disciplines represented by the panel were selected by the peer review leadership team based on nature of the technical ideas that had been proposed and down-selected by DOE EM. As documented below, the peer review panel had significant breadth and gravitas with expertise in chemistry, microbiology, nanotechnology, engineering, geology, geophysics, and other disciplines.

Peer Review Leadership
Brian Looney, Savannah River National Laboratory, Peer Review Chair
Gene LeBoeuf, Consortium for Risk Evaluation with Stakeholder Participation (CRESP) and Vanderbilt University, Peer Review Vice-Chair
Dawn Kaback, Geomatrix Consultants, Peer Review Vice-Chair

Peer Review Participants
The table below provides the names and relevant information for all peer review participants:

Name	Title and Biographical Sentence	Organization	Street Address	Discipline / Assignment	Phone
DOE OVERSIGHT OF PEER REVIEW					
Blaine Rowley	**DOE Project Manager**	**Department of Energy, Office of Cleanup Technologies, EM21**	**19901 Germantown Road Germantown MD 20874**	**Implementation of the congressionally mandated supplemental Funding to protect the Columbia River**	**301-903-2777**
PEER REVIEW COORDINATION					
John Smegal	**Technical Assistance Contracting Specialist**	**The Legin Group**	**12850 Middlebrook Road, Suite 308 Germantown, MD 20874**	**Logistics , contracting and disbursing funding to reviewers**	**(301) 590-0303 ext 15**
Lynn Lefkoff	**Associate, Ten years experience in facilitation and strategic planning.**	**EnviroIssues**	**101 Stewart Street, Suite 1101**	**Technical and meeting support**	**206-269-5041**
Jason Mulvihill-Kuntz	**Technical Specialist -- facilitation and strategic planning.**	**EnviroIssues**	**101 Stewart Street, Suite 1101**	**Technical and meeting support including documentation of discussion and drafting reports**	**206-269-5041**

TECHNICAL REVIEWERS					
Brian Looney	**Peer Review Chair, Senior Advisory Scientist with twenty two years of experience developing and implementing innovative environmental characterization and remediation technologies.**	**Savannah River National Laboratory**	**773-42A Aiken SC 29808**	**Geochemistry, Environmental Technologies / All**	**803-725-3692**
Gene LeBoeuf	**Associate Professor of Civil and Environmental Engineering and representative of the Consortium for Risk Evaluation with Stakeholder Participation.**	**Vanderbilt University, Civil & Environmental Engineering**	**278 Jacobs Hall, 400 24th Avenue South Nashville TN 37235**	**Geohydrology and Modeling / All**	**615-343-7070**
Dawn Kaback	**Principal Geochemist with twenty years experience in innovative characterization and remediation technologies.**	**Geomatrix**	**1401 17th Street Suite 600 Denver CO 80202**	**Geochemistry, Environmental Technologies / All**	**303-534-8722**
Todd Anderson	**Program Manager in the Environmental Remediation Sciences Division of the Office of Biological and Environmental Research.**	**Department of Energy, Office of Science, SC75**	**19901 Germantown Road Germantown MD 20874**	**Environmental Remediation Science / All**	**301-903-5549**
Bruce Wielinga	**Biogeochemist, Member of the Tetra Tech Remediation Strategies Team and the Tetra Tech Technology Transfer Advisory Board.**	**MFG**	**3801 Automation Way, Suite 100 Fort Collins CO 80525**	**Geochemistry / Sr, U, and Cr**	**970-206-4303**
Miles Denham	**Fellow Geologist recognized for innovative applications of geochemistry to environmental remediation.**	**Savannah River National Laboratory**	**773-42A Aiken SC 29808**	**Geochemistry / Sr, U, and Cr**	**803-725-5521**

Paul Deutsch	**Principal Scientist, Phytoremediation Practice Leader .**	**Geomatrix**	**2444 Main Street, Suite 215 Fresno CA 93721**	**Engineering and Phytoremdia-tion/ Sr**	**559-264-6128 ext.126**
Bill Malyk	**Principal Engineer, Environmental Systems Engineering and Design.**	**Geomatrix**	**420 Weber Street North, Unit G Waterloo Ontario Canada N2L 4E7**	**Chemical Engineering / Cr**	**519-886-7500**
Jeffrey J. Daniels	**Professor and Geophysicist, Department of Geological Sciences.**	**The Ohio State University**	**423 Arden Road Columbus OH 43214**	**Geophysics / Cr**	**614-292-4295**
Louise Pellerin	**Head of Research at Green Engineering, Inc., and Adjunct Professor, Stanford University.**	**Green Engineering, Inc.**	**2215 Curtis St Berkeley CA 94702**	**Geophysics / Cr**	**510-704-1566**
David Lesmes	**Program Manager (Geophysicists), Department of Energy Office of Science, Biological and Environmental Research Division.**	**Department of Energy, Office of Science, SC75**	**19901 Germantown Road Germantown MD 20874**	**Environmental Remediation Science / All**	**301-903-2977**
Jess Everett	**Research Scientist who participated in the development of geochemically based protocols for the Department of Defense (e.g., the AMIBA protocol) and the development of combined biological and abiotic remediation concepts (e.g, the BiRD protocol).**	**Rowan University**	**special address – on sabbatical in Sweden**	**Organic Geochemistry / Carbon Tetrachloride**	**46 23 77 8708 (46 is the country code)**

Jackson Ellington	**Research Scientist for the U.S. EPA Laboratory in Athens GA with publications on organic hydrolysis.**	**U. S. EPA, ERD**	**960 College Station Road Athens GA 30605**	**Organic Geochemistry / Carbon Tetrachloride**	**706-355-8204**
Mark Fuhrmann	**Scientist, Twenty-five years experience with behavior of radioactive waste forms and the interactions of contaminants with minerals.**	**Brookhaven National Laboratory**	**Bldg 830, 34 North Railroad St Upton NY 11973**	**Contaminant Biogeochemistr y and Phytoremediati on/ Sr and U**	**631-344-2224**
Ralph Nichols	**Geological engineer and hydrogeologist with fifteen years of experience in field testing of remediation technology and in pump test design and interpretation.**	**Savannah River National Laboratory**	**773-42A Aiken SC 29808**	**Geological Engineering / Carbon Tetrachloride**	**803-725-5228**
Joe Rossabi	**Senior scientist with significant expertise and publications related to environmental characterization, DNAPLs, and advanced remediation technologies (oxidation, biological, and thermal)**	**RedoxTech**	**1006A Morrisville Parkway Morrisville NC 27560**	**Environmental Engineering and Physics / Carbon Tetrachloride**	**919-460-4747**
David Cocke	**Professor, Gill Chair of Chemical Engineering – industry leader in electrochemical water treatment methods**	**Lamar University**	**Chemistry Building Room 101 211 Redbird Lane Beaumont TX. 77710**	**Chemical Engineering / Cr**	**409-880-1862**
Tom Mallouk	**Director Penn State University Center for Nanomaterials**	**The Penn State University, DuPont Professor of Materials Chemistry and Physics**	**224 Chemistry Building**	**Chemistry / Tc**	**814-863-9637**

James (Jim) H. Clarke	**Professor, Remediation of contaminated sites, fate and transport of chemicals and radionuclides, environmental assessment, hazardous and radioactive waste management**	**Department of Civil and Environmental Engineering, Vanderbilt University**	**267 Jacobs Hall, 400 24th Avenue South, Nashville, TN 37235**	**Engineering / Tc**	**(615) 322-3897**
Rod Ewing	**Professor, Structure and crystal chemistry of complex Nb-Ta-Ti oxides, structure and crystal chemistry of actinide-bearing phases, geochemistry of uranium, design and selection of radioactive waste forms**	**Materials Science Engineering Department, University of Michigan**	**H.H. Dow Building, 2300 Hayward Street, Ann Arbor, MI 48109-2136**	**Materials Science / Tc**	**734-763-9295**
Baohua Gu	**Scientist, Fate and transport of metals, radionuclides, and organics; Technetium chemistry; nanomaterials characterization**	**Environmental Sciences Division, Oak Ridge National Laboratory**	**1 Bethel Valley Road, Oak Ridge, TN 37831**	**Chemistry / Tc**	**865-574-7286**
Leonard (Len) C. Feldman	**Professor, Electronic materials, surface and interface science, thin films, epitaxy, nanomaterials science**	**Department of Physics and Astronomy, Vanderbilt University**	**6301 Stevenson Center, Nashville, TN 37235**	**Physical Science / Tc**	**615-343-7273**
C. Andrew Ramsburg	**Professor, Hydrogeology, Modeling, Environmental Engineering**	**Department of Civil & Environmental Engineering, Tufts University**	**200 College Avenue, 113 Anderson Hall, Medford, Massachusetts 02155**	**Engineering / Tc**	

APPENDIX A

Sequestration of ^{90}Sr Subsurface Contamination in the Hanford 100-N Area by Surface Infiltration of an Apatite Solution

Target Plume /Area: Strontium-90 (^{90}Sr) / Hanford 100-N Area

Proposal Title: Sequestration of ^{90}Sr Subsurface Contamination in the Hanford 100-N Area by Surface Infiltration of an Apatite Solution

Proposal Reviewers: Brian Looney, Todd Anderson, Miles Denham, Paul Deutsch, Mark Fuhrmann, Dawn Kaback, Gene LeBoeuf, Bruce Wielinga

Summary Evaluation:
The panel provides qualified support for the infiltration of an apatite-forming solution to sequester ^{90}Sr. The panel supports the systematic approach to sequestering ^{90}Sr, which combines current plans for well injection of apatite solution (calcium-citrate-phosphate) with the infiltration of apatite solution, possible phytoremediation, and natural attenuation. However, some specific technical and implementation issues should be addressed (see below). The panel believes implementation and operation of the proposed sequence of technologies is appropriate to effectively sequester ^{90}Sr (i.e., implementing only one of the technology alternatives would be less effective or ineffective compared to implementing the full suite of technology alternatives). Such a systematic combination of technologies would improve the robustness of the DOE efforts to protect the Columbia River. Further, this approach is consistent with the National Academies / National Research Council recommendation that DOE environmental efforts would benefit from the philosophy of "defense in depth."

The relative benefits of the proposed apatite forming solution versus alternatives (such as the polyphosphate proposed for Uranium in the 300 Area) and the possible design constraints and variations in reagent chemistry to minimize collateral environmental impacts should be provided.

The panel also recommends identifying a hydrologist, geologist or engineer as substantive collaborator this project.

Technical Basis of the Proposal:

Given the dynamic geologic and hydrologic conditions of the Hanford 100-N Area, the panel generally supports the approach to use multiple technologies to address ^{90}Sr concentrations. The proposal regarding Sr-90 sequestration using an apatite barrier is based on sound and valid science. General technical issues for consideration:

- The proposal does not provide a technical basis for the proposed 300-year longevity calculation nor does it provide the technical basis for implementation/endpoint decisions. (see reviewers 2, 3, 5 and 6)
- The proposal lacked a detailed description of the alternative selection process, as well as a compelling argument for choosing this alternative as one of the appropriate choices. Other alternatives that should be considered include:
  - using polyphosphate and calcium chloride
  - using a different injection system (rather than surface infiltration)
  - soil flushing
  - other barrier technologies
  - MNA

  (see all reviews)
- Adequate research and experimental testing has not been done to implement a full-scale project. The current proposal is too focused on the misocosm-level to adequately answer field questions. Consider combining experimental testing and modeling of the apatite infiltration sequence, followed by a field test, to determine the amount of ^{90}Sr that is released from the soil by the relatively high ionic strength of the apatite solution ahead of the forming apatite. If the resulting levels of ^{90}Sr are unacceptably high, measures should be taken to capture mobilized ^{90}Sr in the area between the apatite barrier and the river. Consider clogging and other adverse collateral impacts. (see reviewers 4, 5, 6, and 7.
- Impacts of subsurface heterogeneity on the delivery of apatite solution to the desired depth and spread in the Hanford 100-N Area need to be understood. (see reviewers 2, 3, and 7)
- Consider potential impacts of residual diesel contamination on the apatite formation and ^{90}Sr sequestration process. (see reviewer 7)
- Apatite particle size should be small enough to provide surface area for ^{90}Sr sequestration, but large enough to minimize the potential to mobilize colloidal ^{90}Sr. This can be addressed with geochemical modeling or experimental testing. (see reviewer 2)
- Consider mineral formation resulting from apatite infiltration and how ^{90}Sr is incorporated and held in these minerals. (see reviewers 2, 4, and 6)
- Existing subsurface microbial population could impact the biodegradation rate of the citrate apatite solution, which releases calcium for reaction with phosphate to form the apatite barrier. If the biodegradation rate is too fast, the apatite barrier could form in the upper portion of the Hanford formation, before reaching the concentrated portion of the ^{90}Sr plume. However, if the biodegradation rate is too slow, citrate, phosphate, and other infiltrated nutrients could flow directly into the groundwater and Columbia River. (see reviewer 1)
- Address stakeholder concerns about leaving ^{90}Sr in place using insitu treatment. (see reviewer 5)

- Nutrient-loading could result from injecting and infiltrating a nutrient-laden apatite solution near the river. To address such concerns, consider blending calcium-chloride with the calcium-phosphate. (see reviewers 1, 2, 4 and 5).

Implementation Strategy:

- Proposed budgeted costs are reasonable. Cost-effectiveness is tied to the ability to implement the technologies as proposed.
- The panel suggests conducting shorter, more focused lab tests emphasizing field conditions, as well as some limited controlled field tests to better understand the impacts of subsurface heterogeneity and how the apatite solution would move through the subsurface. Moving through lab tests faster will get to implementability faster. Consider a field component to task 5.
- The implementation schedule for this sequence of complementary technology alternatives likely will not meet the 2008 Tri-Party Agreement milestone to provide a proposed plan. Consider revising the scope to expedite the schedule.
- Use data from apatite well injection work to address some outstanding technical issues regarding apatite delivery and infiltration.

Proposed Performance Metrics:

- The proposal's performance metrics are inadequate and show no specified endpoint. An acceptable endpoint should be identified prior to implementation.
- Specific metrics for development of the deployment strategy are needed.
- The plan for tying results from task to task is unclear.
- Performance metrics should evaluate the implementation of the apatite solution, formation of the apatite barrier, and reduction in ^{90}Sr concentrations.
- Appropriate monitoring program(s) should be identified to track near-term and long-term performance.

Reviewer #1

Target Plume/Area: ^{90}Sr /Hanford 100N Area

Proposal Title: Sequestration of ^{90}Sr Subsurface Contamination in the Hanford 100N Area by Surface Infiltration of an Apatite Solution

Technical Basis of the Proposal:

Is the project or activity based on appropriate and valid science?

Yes. Apatite sequestration is a potential method for sequestering and immobilizing strontium and other contaminants of concern to DOE. Several manuscripts investigating this potential technique have been published in high quality peer-reviewed scientific journals (i.e. *ES&T*). This potential remediation approach has been investigated for Strontium with natural sediments found at DOE sites such as the Hanford 100N.

What is the technical likelihood of the stated-desired outcome?

The stated outcome is to sequester ^{90}Sr permanently within an emplaced apatite barrier formed in the subsurface for the next 300 years. Strontium incorporation into apatite should occur. The amount of apatite required to sequester all of the labile strontium expected to contact the apatite barrier during this time period is as yet unknown. This will be estimated by experimentation. Performance of this remediation technique insitu will strongly depend on the successful installation of the barrier at the optimal locations within the subsurface. Many variables will determine the successful emplacement of the barrier in the subsurface. One such variable of concern is the biodegradation rate of the citrate solution freeing calcium to react with phosphate and form apatite. Citrate degradation will occur but the insitu rate will be difficult to estimate for insitu conditions and may not be a linear function of time. The rate of citrate degradation will determine where in the vertical profile in the subsurface the apatite will form (in addition to matrix effects on flow). A fast degradation rate by indigenous microbes in contact with the infiltrated solutions will result in apatite formation within the upper portions of Hanford formation perhaps prior to the apatite-forming solutions reaching the variably saturated intervals of concern within the 90Sr plume. A slow degradation rate could simply result in a pulse of citrate, phosphate and other nutrients into the groundwater and consequently into the river (depending on the spatial location of the infiltration trench to the river). The preliminary modeling show this to be a possibility and the export to the river bank at the sediment water interface is counted on in the proposal. There is a delicate balancing act here that can be estimated by laboratory experimentation but never fully resolved until implementation in the field. I am concerned that apatite formation may not occur within the subsurface where it is intended to form despite the proposed laboratory experiments which could mimic overall processes but not accurately represent insitu rates of processes. I am also quite concerned about large volumes (1000s gallons?) of apatite-forming solutions to the Columbia River.

Questions:

What are the arguments against emplacing slurried apatite into this area of the aquifer?

How will barrier emplacement be verified insitu? (Geophysics, coring?)

What are the performance metrics for the barrier? ([^{90}Sr]?, other parameters?)

Is the desired goal of the barrier lower [^{90}Sr] concentrations or zero [^{90}Sr]?

How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable?
The proposed infiltration gallery is meant to compliment the apatite injection strategy proposed for areas very near the river at the Hanford 100N area. The infiltration trench for the apatite forming solutions is intended to treat Sr-90 contaminated groundwater within the variably saturated Hanford formation that directly threatens the Columbia River. The proposed project is subject to many variables that will factor into the proper positioning of the barrier within the subsurface. Some of these variables will be constrained via the proposed experiments. Others, such as the rate of biodegradation will only be truly known when field implementation is carried out.

What are the risks or key uncertainties in the proposed action(s)?
A key uncertainty is the inadequate positioning of the barrier due to the insitu vagaries of subsurface flow and an unknown citrate biodegradation rate. Due to the proximity to the river, a major risk is the export of apatite forming solutions (high DOC, nutrients, and phosphate) to the Columbia River, especially considering that several pore volumes of apatite forming solutions will likely be necessary. This also has implications for the phytoremediation project planned for the riparian zone.

Are there clear examples of alternative ideas or proposals that should be considered?
What were the arguments against emplacing pre-formed apatite (slurry or emulsion) into the subsurface rather than relying on so many variables to determine formation and placement of the apatite barrier? The current plan seems much more complicated that it need be.

Implementation Strategy:
The proposed implementation looks like it could be performed relatively cost effectively if it performs as predicted. If not, there could be increased costs to deal with export of apatite forming solutions to the river and any other negative consequences resulting from this.

Proposed Performance Metrics:
There are too few performance metrics proposed. How will the position of the barrier be verified? How will Sr incorporation be verified in the field? Is barrier placement and system performance simply being predicted by computer model?

Summary Evaluation:
See comments to the second question in the Technical Basis section. Because of the proximity to the river, I am concerned about export of apatite solutions (Hi P, Hi DOC, Hi levels of other growth nutrients) to the Columbia River when the experimental tests do not adequately simulate the rates of process as they occur insitu. I think a less complicated solution is in order, one that does not put a highly concentrated nutrient-laden solution so close to the river bank. Perhaps a

possible solution is simply a preformed apatite (slurry or emulsion) barrier without the addition of mobile, labile nutrient-laden solutions that could adversely impact the river.
I cannot recommend this approach due to the very real potential for export of nutrient-laden solutions to the Columbia River.

Reviewer #2

Target Plume/Area: 100N – ^{90}Sr Plume

Proposal Title: Sequestration of ^{90}Sr Subsurface Contamination in the Hanford 100N Area by Surface Infiltration of an Apatite Solution

Technical Basis of the Proposal:
The proposal is based on sound science that has significant uncertainties. Apatite will sequester ^{90}Sr and this proposal is a clever way to emplace apatite in the subsurface without the problems associated with injection of solids. If apatite can be successfully precipitated in the subsurface, then near-term sequestration of ^{90}Sr will be achieved. However, one of the goals is to precipitate sufficient apatite to continue the sequestration process for 300 years. There are two major uncertainties with the amount of apatite required that are not addressed in the proposed work.

1) Does reaction of constituents other than Ca, Sr, and Mg eventually render the apatite surface inert to Sr? It is thermodynamically favorable for barium, ferric iron, and lead to form insoluble phases with phosphate. This could occur at the surface of the apatite making it less reactive to Sr. The concentration of these in groundwater are low relative to Ca, Mg, and Sr, but over time they may affect the surface chemistry of the apatite and reduce Sr adsorption.

2) How much surface area of apatite is required to achieve effectiveness for 300 years? The authors discuss the mass of apatite required to sequester ^{90}Sr for 300 years, but presumably this is based on the assumption that all of the apatite reacts. A better measure of the amount of apatite required is the surface area. The surface area is dependent on crystal size and shape. At small total surface areas, the interiors of crystals may never react and more apatite would be needed.

Another uncertainty, related to the size of crystals, is the potential of colloidal mobilization. Particles 100 nm in size, or less, are potentially mobile in aquifers as colloids. Thus, the possibility that apatite crystals could be a vector to enhance mobility of ^{90}Sr should be considered.

Implementation Strategy:
It is difficult to evaluate the implementation strategy because there were no details on how infiltration would be done. Most of the proposed tasks are to test and optimize infiltration. However, they do not make a compelling case for why infiltration needs to be done rather than emplacing the apatite in other ways (e.g., injection). The case seems to be based on 2 factors -- that the vadose zone is where much of the contamination is and that infiltration would extend the time period for effective application of the technology. Does most of the contamination in the vadose zone ultimately pass through the unsaturated zone? If so, then sufficient apatite in the saturated zone should reduce concentrations of ^{90}Sr reaching the river. If the only real benefit is extending the optimal time of application, does this truly warrant the additional cost and uncertainty of using infiltration? The budget seems reasonable for the 5 tasks they propose.

Proposed Performance Metrics:
The proposed technology is likely to be an improvement over pump-and-treat, whether infiltration is an improvement over direct injection is unclear. The main measurable parameter that would document performance is long-term measurements of ^{90}Sr at the river.

Summary Evaluation:
The idea of injecting a solution that biodegrades and ultimately causes precipitation of apatite is a clever method of emplacing apatite in the subsurface. There are uncertainties that should be addressed by the authors with simulations or experiments before field deployment. The major weakness of the proposal is the lack of a compelling reason why infiltration needs to be done, together with or instead of, injection into the saturated zone.

Reviewer #3

Target Plume/Area: Strontium-90 Plume - 100N Area Hanford, WA

Proposal Title: Sequestration of Strontium-90 Subsurface Contamination in the Hanford - 100N Area by Surface Infiltration of an Apatite Solution

Technical Basis of the Proposal:
The authors propose laboratory and modeling tasks to develop and strategy for infiltration of an apatite forming solution to aid in sequestering ^{90}Sr in the vadose zone. Previous work by Hanford staff has shown this technology to be effective at sequestering ^{90}Sr and has recommended injecting a similar solution into the saturated zone to sequester the chemical. The project is based on appropriate and valid science and is a key component of other technologies proposed to stabilize/remediate the riparian zone of the Columbia River.

Uncertainties associated with this study will be how effective the solution can be infiltrated into the vadose zone. The proposal present excellent science and modeling tasks but does not address the solution might be distributed through a heterogeneous vadose zone. Task 5 should include a small field component that would address this issue.

Implementation Strategy:
The implementation strategy appears to be appropriate for the objectives of this study. The laboratory and modeling tasks are very good and it appears that the timing is valid. The implementation schedule of this activity and the phytoremediation tasks seem to be a bit conflicting. Budgets appear to be adequate for the proposal as written; however, if a field study is added additional budget would be required.

Proposed Performance Metrics:
Apatite sequestration of ^{90}Sr will be a significant improvement of the existing pump and treat system. According to background information, the pump and treat system is not effective in remediating the riparian zone of the Columbia River. The proposed technologies combined with the phytotechnologies will be effective in reducing the mass of contaminants in the soil and groundwater associated with the 100-N portion of the river.

Summary Evaluation:
In summary, the proposal provides a reasonable approach to remove ^{90}Sr from the system. ^{90}Sr sequestration by apatite has been show to be effective and might be the only treatment that is needed in the riparian zone of the River (Phytotechnologies are proposed as a polish to injection and infiltration of the apatite forming solutions). The main limitation of this proposal is the primary focus on laboratory and modeling studies for developing an injection strategy. To effectively implement the injection option, a better understanding is needed of how the solution

will infiltrate (fingering etc) into and through the heterogeneous materials that comprise the subsurface. Once the unsaturated flow of this area is better understood then a delivery system could be designed accordingly.

Reviewer #4

Target Plume/Area: ^{90}Sr in the 100N area

Proposal Title: Sequestration of ^{90}Sr subsurface contamination in the Hanford 100N Area by Surface infiltration of an Apatite Solution

Technical Basis of the Proposal:
This proposed project provides experimental and modeling information from which a strategy will be developed to infiltrate an apatite forming solution into a 300 foot long area near the bank of the Columbia River where ^{90}Sr is outcropping. Preliminary work to develop the method has been published. Now experiments and modeling are needed in the context of different moisture regimes and with site specific soils. The science that is available is valid and this proposed project expands on that basis. The concept of the apatite formation and Sr incorporation in it is sound. I find the idea of using citrate complexed Ca that is biodegraded to slowly allow Ca to be available for reaction with the phosphate, to be very clever. As a result this seems to be a reasonable and practical approach to an otherwise intractable problem.

This work will develop a better understanding of key processes and parameters in order to implement a full-scale remediation. As such the proposal is well thought out and certainly appropriate. Many of the key risks to the actual remediation will be assessed in the proposed work. But there are several that are especially important. As pointed out in the proposal, some ^{90}Sr will be eluted from the soil by the relatively high ionic strength solution that forms the apatite. This contaminant, and possibly others co-existing on the soil, will move ahead of the forming apatite. This slug may be lost to the river or intercepted by the phytoremediation project. The solution, as stated in the proposal is to do two infiltrations; the first at low concentrations to minimize Sr remobilization, followed a month later by the full strength solution. This sounds reasonable and is a good approach but I do not see where it will be tested experimentally. I suggest that the final task of this project be combined modeling and experimental work to try to replicate this process in 2-D, including the two stage infiltration and following ^{90}Sr concentrations in the effluent. In fact, it may be more appropriate to include a field study as the final step if lab tests work well. If more ^{90}Sr is eluted than is acceptable, it may be necessary to install low-flow pump and treat temporarily to catch the mobilized contaminant unless it is thought that the phytoremediation zone can cope with the additional influx. As part of this experiment it will also be important to look for Sr associated with particles of apatite that are small enough to be mobile. One of the papers suggest particles can be nanoscale and as such they may be mobile. Given the flushing action provided by different stages of the river this possibility could be important and should be examined.

Care must be taken to ascertain what minerals are formed and how Sr is retained in them.

I doubt that there are other alternatives that haven't been considered. The one possibility is incorporation of zeolite into the shallower contaminated soil to enhance the Kd or a permeable reactive barrier of similar materials.

A small point…materials other than ceramic for the pore water samples may be desirable because of sorption of Ca and Sr on ceramic.

Implementation Strategy:
The sequence and timing seem OK. Cost seems reasonable for this proposal and if the full-scale infiltration works out, very significant saving in money, river quality and PR will be attained.

Proposed Performance Metrics:
The proposed work hopefully will lead to a very much improved approach compared to well injections by providing better distribution of reagents in a difficult groundwater regime. Yes it should provide improved protection of the river. As suggested, the key is to demonstrate the full concept in an experimental and modeling 2-D simulation.

Summary Evaluation:
This proposal clearly outlines a very appropriate approach to developing data and a model that can then be used to better understand and then implement an infiltration based remediation that should work to help retain ^{90}Sr that is flowing to the river. The proposed method is new, very promising, and worth investing in.

Reviewer #5

Target Plume/Area: 100 N Area

Proposal Title: Infiltration of Apatite Solution for Sequestration of ^{90}Sr

Technical Basis of the Proposal:

1. The project is based on appropriate and valid science; phosphate is known to be a good alternative for sequestration of Sr; however, issues exist related to delivery (i.e. heterogeneity), scaling, and long-term effectiveness (as the apatite ages is it no longer effective in capturing Sr as it flows into the barrier?) *How was the 300-year long longevity calculated? What is the basis for this?*
2. The likelihood of the desired outcome is fair to good, but issues described above could impact performance. What is an acceptable endpoint? This should be defined prior to implementation.
3. This could be a good systems approach when combined with injection below the water table.
4. Approach is reasonable and practicable, but must address issues described above or else it won't be successful and will be like the ISRM.
5. Key risks and uncertainties relate to the delivery, scaling, long-term effectiveness, potential for Sr mobilization, presence of co-contaminants affecting performance. *Can citrate increase Sr mobilization? Is there any information on the microbial population? Is there a possible stakeholder concern about leaving the contamination in place? There is some concern about colloidal apatite that could migrate through the aquifer. Need small grain size to have sufficient surface area, but could have mobilization. If grain size is large, may not have surface area to sequester the Sr. What is concentration of Sr as trace element in citrate being added? This could add non-radioactive Sr to the system that would compete with* ^{90}Sr.
6. Alternatives, such as polyphosphate as proposed in 300 Area or soil flushing do exist. Little evidence of how this alternative was selected as compared to other alternatives was presented. Soil mixing with zeolite or apatite might also be possible; soil flushing has the issue of controlling the release Sr and recovering it. MNA, sheet piles or slurry walls were also identified by ITRD; phytoremediation is also an alternative.
7. This technology was previously recommended by the ITRC as one tool in the toolbox.

Implementation Strategy:

The sequence and timing of activities is appropriate; full-scale implementation will require significant further testing and design especially related to delivery (heterogeneity and scaling); resources will need to be committed to address this issue. Consider including some limited field testing to address delivery issues, so that this does not become the next ISRM.

Currently there is not sufficient evidence that the technology can be implemented cost effectively; this project is a *"proof of principle"* test and will require significant further testing, especially related to scale up prior to implementation

- Does this schedule meet the 2008 milestone? Expediting this schedule would be helpful.
- Budget is appropriate.

- Consider incorporation of data from injection work to answer questions, such as crystal size, aging, etc.

Proposed Performance Metrics:
(Does the proposed project or activity represent a significant improvement compared to the baseline? Does the project improve the protection of the Columbia River now or in the future? Are there measurable parameters that would document performance? Are these included in the proposal?)
- The project represents an improvement compared to the current baseline of pump and treat upgradient, as it directly addresses Sr contamination near the river.
- The project attempts to protect the Columbia River in the near term; however, the technology will not be ready for implementation for a number of years.
- Performance of the technology will be measured by the current monitoring system, but long-term goals must be developed.

Summary Evaluation:
Overall, recommend this technology be implemented, only if the project can address the issues described above. This will require a larger budget and more time, because the project should include field implementation to understand the effect of heterogeneity and delivery of the reactant. Consider combining this project with the polyphosphate in the 300 Area and perform the tests in the laboratory side by side for both uranium and strontium. There may be some economy of scale with this approach, leaving some funding to address delivery and scaling, which are issues for all of the insitu remediation projects. Consider better integration of hydrology/geology into the proposal to enable a successful delivery strategy.

Reviewer #6

Target Plume/Area: 100N Area

Proposal Title: Sequestration of Sr-90 Subsurface Contamination in the Hanford 100N Area by Surface Infiltration of an Apatite Solution

Technical Basis of the Proposal:
Is the project or activity based on appropriate and valid science?
Yes, this effort will lead to an increased knowledge base of Ca-apatite formation in variably saturated media – data sorely needed to further understand how infiltration methodologies should be employed.

Concerns follow:
Task 1 – Apatite Formation at Low Water Saturation (Szecsody/PNNL)
- Lack of investigation of apatite formation influence on porosity at low water saturation.

Task 2 – Infiltration at Variable Ca-citrate-PO4 Concentration (Szecsody, Rockhold/PNNL)
- Subtask 2.3 examines the influence of heterogeneities in 1-D columns including a high-K zone and a low-K zone in the center of the column. How will this information be used to assist in designing 2D experiments, 1D and 2D simulations, and the field to modify "to some extent" the infiltration strategy? This remains rather unclear.

Task 3 – Apatite Sr Capacity and Uptake Rate (Moore/SNL)
- Subtask 3.2 experimentally examines the rate of Sr substitution into Ca-apatite through a series of long term batch studies at different temperature (22^{o}C, 42^{o}C, 62^{o}C, and 82^{o}C). Here, the different temperature studies are at temperatures in excess of the GW temperature (15C); as such there is real concern regarding extrapolation of the activation energy data to the lower temperatures. Task should include at least one to two temperatures at or below the GW temperature. Further, will solid phase sampling at period time intervals to 1 year include both solid phase apatite and mixtures of sediment and apatite? How will the 1 year data be extrapolated to the 300 year mark (i.e., what statistical methods will be employed to investigate the expected range in model parameters?).

Task 4 – Simulation of Apatite-Forming Solution Infiltration (Rockhold/PNNL)
- Designing the field-scale injection strategy (Task 4.3) will be accomplished with a combination of experimental data (batch, 1-D, and 2-D) and simulations. Details of how this will be accomplished, however, are lacking. What are the most important model parameters for simulation? How will these be determined in the field? Again, what type of modeling/simulation work

Task 5 – Apatite Spatial Distribution from Surface Infiltration (Oostrom/PNNL)
- Good to focus on critical, high-K formations for apatite precipitate, but what is the variability in water saturations to be examined in these formations; further, what is the range of conductivities to be examined in this portion of the study? Can this be done in the field?

What is the technical likelihood of the stated-desired outcome?
Good, if a more methodical approach is used to interconnect individual project tasks.

How does the project fit in with the totality of proposed activities for the target contaminant/plume?
The proposed TPA agreement is to emplace (inject) a 300-ft wide apatite barrier in the deeper (water-saturated) sediments near the Columbia River. This proposed work would develop an infiltration method for apatite placement in unsaturated sediments, which would be applied to shallow Sr-90 contamination in the Hanford 100N area near the Columbia River shoreline, thus complementing the deep-well injection.

Is the proposed approach reasonable and practicable?
Yes.

What are the risks or key uncertainties in the proposed action(s)?
Key risks and uncertainties lie in (i) inability to provide homogeneous apatite barrier for Sr-90 sequestration; and (ii) the potential for Sr-90 to be remobilized due to influx of high ionic-strength infiltration.

Are there clear examples of alternative ideas or proposals that should be considered?
See above comments.

Implementation Strategy:
Is the sequence and timing of activities appropriate?
Yes, the five task implementation strategy appears to be relatively well-sequenced..

Can the technology be implemented cost-effectively?
Yes, the budget appears appropriate for the stated scope of laboratory and simulation activity.

Is the budget and level of effort appropriate for the proposed work?
Yes.

Proposed Performance Metrics:
Does the proposed project or activity represent a significant improvement compared to the baseline?
Yes. Two primary contributions here: (i) additional experimental data on apatite formation/precipitation under variably saturated conditions; and (ii) incorporation of a multi-component ion-exchange model into STOMP to enhance the predictive capability of the model, and provide for improved guidance for infiltration strategies.

Does the project improve the protection of the Columbia River now or in the future?

Likely, yes. This project develops an infiltration strategy for apatite emplacement will supplement the current plan for injection of the Ca-citrate-PO4 solution. The current implementation plan is to inject low concentration solution in FY06, then high concentration solutions in FY07. The proposed project will develop the infiltration strategy by the end of FY07 for implementation in FY08.

Are there measurable parameters that would document performance?
Yes. The two main deliverables are: (i) laboratory data at multiple scales (batch, 1-D, 2-D) that will assist in development of an infiltration strategy, and (ii) development of a simulation tool to describe apatite reactions during solution infiltration and Sr-90 response.

Are these included in the proposal?
Yes.

Summary Evaluation:

Overall, a well-thought out proposal that brings both improvements in our knowledge base of the influence of variably-saturated conditions on apatite formation/precipitation, effect on permeability, and improvement of a transport/reaction model for simulation. Can lead to improved protocols for infiltration strategy if additional methodologies are employed.

Reviewer #7

Target Plume/Area: Sr / 100 N Area

Proposal Title: Sequestration of Sr-90 Subsurface Contamination in the Hanford 100N Area by Surface Infiltration of an Apatite Solution

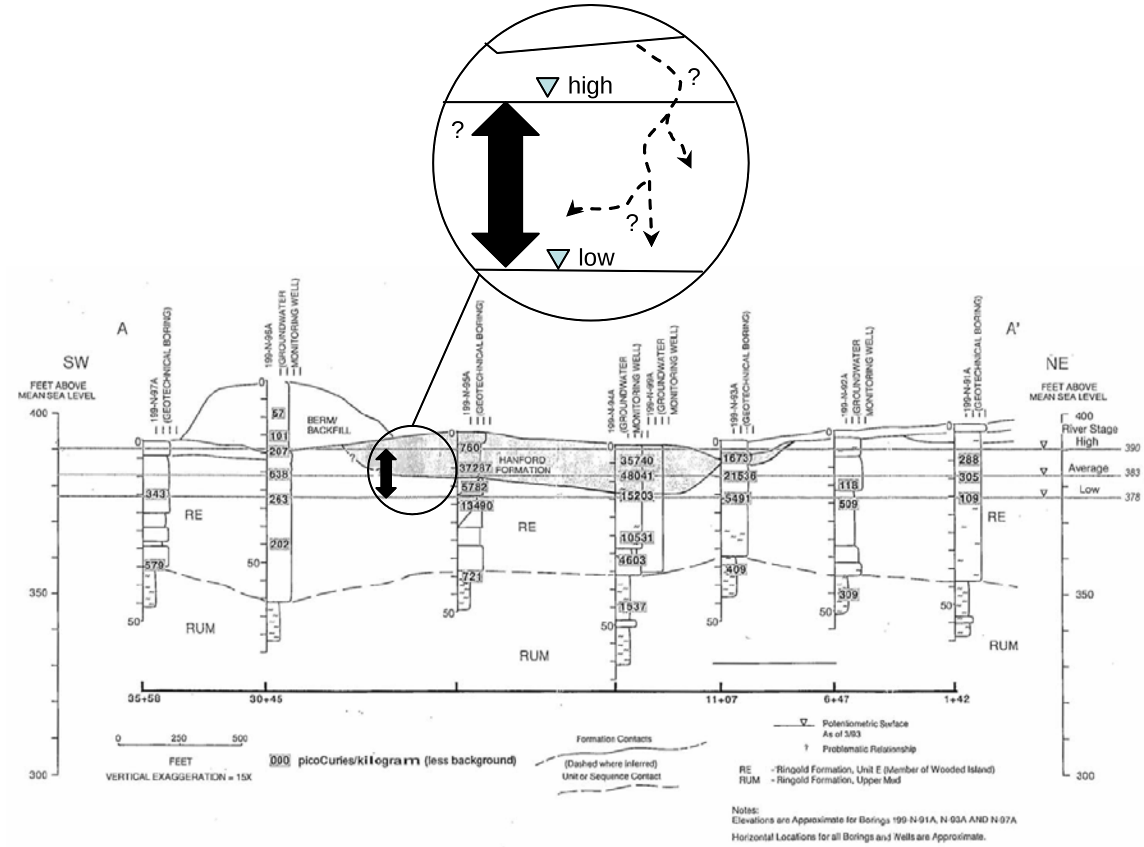
Technical Basis of the Proposal:
General Approach

This project is generally consistent with previous peer reviews and recommendations and the follow up research efforts.

ITRD Technology Evaluation
100-NR-2 Operable Unit

Technology	Conclusion	Recommendation
Monitored Natural Attenuation (MNA)	May be appropriate for portion of plume far from the river, but will not limit current discharges of ^{90}Sr from N-Springs.	Should be examined in more detail when establishing Long-Term Stewardship protocols.
Soil Flushing	Likely to be effective in removing ^{90}Sr in the shortest time frame.	Should be examined in more detail with regulators.
Phytoremediation	May be the best option for controlling current releases at the river; leaf litter control may be an issue.	Needs more analysis.
^{90}Sr stabilization by phosphate injection	Design studies were insufficient to support recommendation of the option.	Re-examine this option after the Tanks Focus Area work is completed.
Barrier technologies (clinoptilolite and sheet pile/cryogenic)	Installation is considered feasible. Bank is stable and erosion potential associated with construction is considered negligible.	Precautions during construction should minimize potential damage.

Injection of the citrate-phosphate solution below the water table has been selected and approved by the regulators and stakeholders and is scheduled to be implemented. This proposal is to add an infiltration of apatite forming solution to the injection consistent with the following:
"The majority of the 1,500 curies (Ci) of 90Sr remaining in the unsaturated and saturated zones in the 100-N Area as of 2003, is present in the vadose zone above the aquifer. An estimated 72 Ci of 90Sr are contained in the saturated zone, and approximately 0.8 Ci are in the groundwater. Data from soil borings collected along the riverbank indicate that 90Sr concentrations in soil reach a maximum near the mean water table elevation and then decrease with depth." Thus, infusion of solution in the deep vadose zone appears reasonable and may be as useful as, or better than, the planned injections from the standpoint of desired geometry of treatment.



General Technical issues to be considered include:

Will the reagents efficiently pass through the vadose zone to the desired depth. Since the solution is concentrated this may not be an issue.

Heterogeneity – the solution will tend to finger and migrate in narrow pathways and then, since it is an aqueous solution and denser than water, it may not spread throughout the desired treatment zone at the capillary fringe or groundwater.

Salting out, or the potential mobilization of Sr and the edge of the process where a high ionic strength sodium solution exits the treatment zone – this was identified in the earlier peer reviews and is a potential consideration in the design and sequencing of fluids to be delivered (or in where they are delivered).

Impact of diesel residual on process – a large past diesel oil spill has left a portion of the site groundwater in a chemically reduced state and with relatively high levels of dissolved iron (according to the treatability test plan for the injection). Iron levels were higher in the past, but appear to be significantly lower in recent data, however. While this may be less of an impact in the vadose zone, there are still some potential issues – is the area between the high and low water level an organic "smear zone" in affected portions of the site? If so, what are the potential negative (or positive) benefits of residual hydrocarbon? How would this impact the citrate degradation and apatite formation? Would the iron impact apatite mineralogy or compete for sorption sites? This work will need to be done at low water level and with a consideration of water level trends.

The schedule and costs appear reasonable.

Implementation Strategy:
Generally good.

On page 10 the proposal notes that solution density will have little impact on distribution because of capillary controls in the vadose zone. This is dependent on the lithology and is unlikely to be the case in coarse grained material like the vadose zone near the Columbia River. The plan is very meticulous with large emphasis on mesoscale lab studies. It is not clear why both 1D and 2D experiments are performed at the level proposed (the proposers note that they build on each other, but apatite solution injection studies have already been done to support the injection work). It is not clear that the mesoscale studies are going to tell the site anything about the controlling heterogeneities at the site. DOE may not need a large mesoscale test to show that the solution will be controlled by heterogeneities, Consider shorter more focused lab campaign and more emphasis on the controlling field conditions. Perhaps consider some field testing in task 5 rather than more mesocosm studies.

Proposed Performance Metrics:
Few Columbia River Performance metrics are included since the focus in lab mesocosms. I recommend thinking about the Columbia River and adjusting the hypotheses so that the studies will result in performance metrics that can be used to judge the deployment of the reagent, the formation of apatite, and the reduction in Sr flux. How will field tests be monitored and decisions about mending made?

Summary Evaluation:
This is an interesting and meritorious idea that has the potential to reduce the flux of Sr to the Columbia river in a measurable way. Several suggestions are provided in the specific topics.

Reviewer #8

Target Plume/Area: 100-N Riparian Zone

Proposal Title: Sequestration of Sr-90 Subsurface Contamination in the Hanford 100N Area by Surface Infiltration of an Apatite Solution

Technical Basis of the Proposal:

Is the project or activity based on appropriate and valid science? Science is appropriate and valid for the sequestration of Sr within the vadose and saturated zones adjacent to the Columbia River. Experimental design is sound and the stated methods of analysis reasonable.

What is the technical likelihood of the stated-desired outcome? Based on the supplemental literature provided, it would appear that this technology has a reasonably good potential to sequester ^{90}Sr and could provide additional protection of the Columbia River.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? The technology fits well with the systems approach to reducing Sr discharge to the Columbia River. If this work is successful at providing proof-of-principle, this could expand the ability of DOE to remediate the site and protect the river.

Is the proposed approach reasonable and practicable? The proposal is entirely lab/bench-scale experimental, and thus issues of scaling to full-scale treatment will need to be addressed at a later date. In addition, it is unclear from the proposal to what extend site-specific soils will be incorporated into the experiments. It would seem that this would be an important component of the work to validate the technology for use at this site.

It is also somewhat unclear how data gathered during various tasks will be extrapolated to predict results for field implementation. For example, Task 1 will focus on evaluating citrate biodegradation rates as a function of water content and microbial population. Very little detail is provided as to how the microbial populations will be characterized, and/or how this can be related to field conditions. From the information provided, it appears that there is very little known about the microbial ecology of the site and this data gap will likely make extrapolation of batch results to field-scale predictions very difficult.

What are the risks or key uncertainties in the proposed action(s)? One key uncertainty is whether current laboratory based approach can be realistically scaled to field-scale implementation without significant additional testing, which will translate to delays in technology deployment. In addition, the addition of citrate, which is an excellent chelator of divalent metal ions, could have as yet unforeseen consequences. It will therefore be important to design a robust laboratory monitoring and analytical program to provide the most accurate data feasible regarding possible citrate affects.

Are there clear examples of alternative ideas or proposals that should be considered? Incorporation of a field-scale component would greatly aid in the evaluation of the technology in the heterogeneous conditions prevalent at the Hanford site.

Implementation Strategy:

Is the sequence and timing of activities appropriate? Activities specified in the proposal seem appropriate.

Can the technology be implemented cost-effectively? If the technology is shown to be effective at stably sequestering ^{90}Sr over the long-term, and is ultimately deployed in the 100-N Area, it could be a very cost-effective treatment strategy as compared to the existing P&T system.

Is the budget and level of effort appropriate for the proposed work? Budgetary analysis is better addressed by those familiar with costs typically associate with this type of work at national labs.

Proposed Performance Metrics:

Does the proposed project or activity represent a significant improvement compared to the baseline? This technology if successfully implemented would be a significant improvement over the current P&T system both in terms of protection of the river and lifecycle costs.

Does the project improve the protection of the Columbia River now or in the future? As above, if determined to be implementable, the technology evaluated in this proposal would significantly improve the protection of the Columbia River as compared to baseline P&T system.

Are there measurable parameters that would document performance? The experimental design is generally well thought through and appropriate analyses are included to validate the performance of Sr sequestration at the bench-scale. However, as discussed above, very little detail is provided with respect to assessing the microbial component in the studies, which is key to understanding biodegradation, and how what is measured in small batch systems can be scaled successfully to account for the likely heterogeneous microbial populations found in the field.

Are these included in the proposal? In many cases yes, in other instances these are not clearly defined.

Summary Evaluation:

Generally a good research proposal designed to provide a proof-of-principle for *insitu* strontium sequestration via the infiltration of a calcium-citrate-phosphate solution with the concomitant precipitation of apatite. The most significant shortfall of the proposal, from this reviewer's perspective, is the lack of a field-scale component. The batch tests and bench-scale 1-D column studies will no doubt provide useful information, but it is unclear how realistically these data can be scaled to predict results of infiltration at full-scale.

APPENDIX B

Phytoremediation – Treatability Study along the 100-N Riparian Zone

Summary Review

Target Plume /Area: Strontium-90 (Sr-90) / Hanford 100-N Area

Proposal Title: Phytoremediation – Treatability Study along the 100-N Riparian Zone

Proposal Reviewers: Brian Looney (lead), Todd Anderson, Miles Denham, Paul Deutsch, Mark Fuhrmann, Dawn Kaback, Gene LeBoeuf, Bruce Wielinga.

Summary Evaluation:
The panel supports the proposal with some qualifications that need to be addressed. Specific issues identified by the panel relate to the sequencing of technologies, identifying performance metrics, performing tests to better understand potential collateral impacts of the phytoremediation system, and ensuring estimated lifecycle costs are realistic.

Technical Basis of the Proposal:
The panel generally supports the use of phytoremediation technology as a component of a good systems approach to addressing Sr-90 contamination. The proposal builds on valid and appropriate science regarding Coyote willows (*Salix exigua*) and their ability to remove Sr-90.

Technical issues for consideration:

- Determine effective and appropriate sequencing of apatite infiltration and phytoremediation technologies. Consider whether chemicals in the apatite solution could adversely impact Coyote willows during or after infiltration. (Reviewers 1, 2, 4, 5, 8)
- If the ratio of calcium to strontium in the groundwater increases as a result of apatite infiltration, the willows will take up less Sr-90. (Reviewer 2)
- It is uncertain how much Sr-90 could be removed by the willows over a distinct period of time. Phytoremediation seems to be a good technology from a public relations perspective, but care should be taken to avoid over-promising how much Sr-90 can be removed using this technology. Phytoremediation should be referred to as a "polishing step," and will likely extract a relatively small amount of Sr-90. (Reviewers 1, 8)
- Conducting a test in a contaminated ("rad") site, to determine the amount of Sr-90 that can be removed by the willows.
- Fertilizer application issues, such as the amount, timing, and fertilization rate, must be clarified. (Reviewers 5, 6)
- Collateral release issues relating to the management and control of the system need further clarification (e.g., leaves, twigs and branches, food web vectors, fire control, etc.). (Reviewers 1, 3, 6) Stakeholders desire some assurance that the release of contaminated material will be managed. (Reviewer 6)
- Quantify the distribution of the willow root system. (Reviewer 3)

- Propagating willows in rip-rap material along the river could be difficult. (Reviewer 7)
- Describe harvested biomass transport and disposal plans.
- Identify the basis for the proposed phytoremediation treatment period of between 5-30 years (i.e., clarify the “exit strategy”). (Reviewer 7)
- Compare the effectiveness of mixing zeolite, apatite, or other adsorbent into the soil in the riparian zone as an alternative to phytoremediation. (Reviewers 1, 5, 6)
- Implementing apatite sequestration at a low river stage as an alternative to phytoremediation. (Reviewer 7)
-

Implementation Strategy:

- The implementation schedule is reasonable.
- Phytoremediation technology is relatively inexpensive; however, proposed budgeted lifecycle costs for effectively carrying out phytoremediation are too optimistic. (Reviewer 7)
- Test phytoremediation in either a rad site or in both a rad and nonrad site. A test in a nonrad site alone would not be effective. Tests could be performed on existing stands of willows depending on availability. (Reviewer 4)
- Identify how the apatite barrier is functioning before implementing phytoremediation. However, consider the benefit and ability of the willows to capture Sr-90 that is released as a result of initial apatite infiltration.
- Ensure that Sr-90 in the groundwater flows through the phytoremediation site.
- If the apatite barrier is performing perfectly, phytoremediation may not be necessary. Phytoremediation provides “defense in depth” coverage in case the apatite barrier fails. (Reviewer 2)
-

Proposed Performance Metrics:

- Although the proposal discusses plans to analyze harvested biomass for Sr-90, no end point criteria for removing willows and discontinuing phytoremediation are identified. The cessation of the system should be based on a quantitative goal, so it is clear when it is no longer needed. These should be examined in the treatability study. (Reviewers 1, 7)
- In addition to measuring Sr-90 in harvested plant material, groundwater monitoring and sediment sampling should also be considered. (Reviewer 1)
- The effectiveness of willows to take up Sr-90 relative to the amount of Sr-90 reaching the river needs to be monitored throughout the lifetime of the phytoremediation system.
-

Reviewer #1

Target Plume/Area: Strontium-90/Hanford 100N Area

Proposal Title: Phytoremediation – Treatability Study along the 100-N Riparian Zone

Technical Basis of the Proposal:

Is the project or activity based on appropriate and valid science?

Phytoremediation is a potential remediation strategy for a variety of contaminants. However, some of the best-known plants used for remediation purposes are not indigenous to the sites where phytoremediation is a considered possibility and are objectionable on that point alone. Such is the case with the proposed phytoremediation project at the 100N area. Coyote willow seems to be an attractive, native plant for possible phytoremediation but does not appear to be a "accumulator" of strontium incorporating Sr into cell tissues in similar ratios as found in the pore water. The evidence presented indicates that Sr accumulates in cell walls and woody tissues of the plants in ratios very near those observed in the ground/pore water. This is not an optimal plant for phytoremediation for Sr but it is native to the region and that is a valid approach.

What is the technical likelihood of the stated-desired outcome?

The outcome appears to be that the coyote willow will act as a final "barrier" to preventing the entry of Sr-90 present in the sediments directly within the riparian zone and perhaps from further upgradient into the Columbia River. From the given data and assuming optimal growth and an accumulation of a Sr content similar to the groundwater concentration, how much Sr-90 (Ci) would be "harvested" each season compared to what is entering into the Columbia River now? In other words, what is the Sr-90 uptake capacity of this remediation technique? This seems to be a crucial calculation and would assess the potential effectiveness of this proposed technique and provide a benchmark, backed up by actual measurements of biomass Sr-90 to work with in the future.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable?

Two upgradient apatite emplacement techniques are planned to deal with Sr-90 found in the subsurface further upgradient. Phytoremediation in the riparian zone is planned as a final barrier/filter to prevent the entry of Sr-90 from the riparian zone into the river. There is logic to this approach. However, coyote willow does not appear to be a hyperaccumulator of Sr and the infiltration gallery for apatite solutions directly upgradient may leach solutions into the riparian zone and produce conditions preventing optimal growth of coyote willow and/or producing transient fluxes (initially) of high Sr-90 groundwater that will not be taken up completely by the proposed phytoremediation scheme.

What are the risks or key uncertainties in the proposed action(s)?

If the coyote willow proves capable of accumulating Sr-90 to detectable levels some of the key risks are the loss of willow to grazing and/or from detachment from the riverbank and transport downriver.

Another risk is that the injected apatite solutions from the infiltration gallery immediately upgradient on the river will leach to the riparian zone creating conditions that may be incompatible with robust growth of coyote willow or producing Sr-90 fluxes that the willow will not be able to take up completely.

Are there clear examples of alternative ideas or proposals that should be considered?
Emplacement of solid apatite "gravel" just under, behind or around the riprap in the riparian zone? Is this a possibility?

Implementation Strategy:
The budget seems appropriate to the level of proposed work.

Proposed Performance Metrics:
Harvesting of coyote willow is mentioned in the proposal and there is mention of analysis of the biomass for Sr-90 content over a period of about 4-7 years. Just to re-iterate, these biomass analyses need to be coupled with a groundwater monitoring and sediment sampling program to validate the performance of the phytoremediation project. The effectiveness of Sr-90 accumulation in the plants relative to Sr-90 export to the river needs to be examined and tracked throughout the lifetime of the phytoremediation project.

Summary Evaluation:
The proposed project will assess the feasibility of using coyote willow as a phytoremediation agent to accumulate and block transport of Sr-90 from the riparian zone to the Columbia River. The experiments planned will illuminate some of the unknowns associated with Sr-90 uptake by coyote willow and its growth characteristics in the 100N area. I find that there are logical reasons for trying a phytoremediation approach in the 100N area but I question whether this approach will result in the recovery of a significant amount of Sr-90. If no significant accumulation of Sr-90 in coyote willow can be demonstrated after several harvests (3-4) then the project should end. The overall phytoremediation approach seems reasonable but some thought needs to be placed on verifying that the phytoremediation is indeed working once emplaced. A key performance monitoring metric could include the Sr-90 content of the harvested biomass relative to the Sr-90 export to the river. There was some mention of this performance monitoring in the proposal but this needs to be emphasized more strongly. I recommend that this proposal go forward.

Reviewer #2

Target Plume/Area: 100N – Sr-90 Plume

Proposal Title: Phytoremediation – Treatability Study Along the 100-N Riparian Zone

Technical Basis of the Proposal:
The proposal investigates planting of Coyote Willow between the apatite emplacement and the river as a "polishing" step in the removal of Sr-90. In preliminary studies Coyote Willow seems to effectively uptake Sr, so there is a sound scientific basis. However, none of the previous work addresses Coyote Willow growth and uptake of Sr-90 in conditions expected during and after apatite emplacement. In the apatite infiltration experiments concentrations of Ca-citrate up to 100mM may be used. Do these concentrations or other chemical changes induced by the apatite emplacement method affect plant health and Sr-90 uptake? For example, the citrate and its degradation products, as well as the phosphate, may increase dissolved aluminum and ferric iron concentrations significantly. Does this affect plant health and uptake? The high concentrations of calcium to be used will affect uptake of Sr-90. It is unlikely that all calcium will immediately react with phosphate and unreacted calcium will raise the Ca/Sr ratio. Previous results show that the Coyote Willow will take up Ca and Sr in the same ratio as in groundwater. If the Ca/Sr ratio of the groundwater is increased by the apatite infiltration, the plants will take up less strontium, and hence, less Sr-90.

A similar reduction in Sr-90 uptake might occur if the Ca-citrate solution contains small concentrations of stable strontium. If the Ca-citrate solid has 10 mg/kg stable Sr, then the 29% solution will have 2.9 mg stable Sr per kg of solution. This concentration is likely to be at least 10 times higher than the natural background concentration of stable Sr. Thus, it will raise the ratio of stable Sr to Sr-90 by a factor of 10, reducing uptake of Sr-90 by a factor of 10. This is an easy uncertainty to address by analyzing the Ca-citrate solution for stable Sr.

Do the chemicals used in the apatite emplacement affect the microbial community around plant roots, in turn, affecting Sr-90 uptake? It might be prudent to answer these questions prior to planting a test plot.

Implementation Strategy:
The plan is to put the test plot in ASAP. It might make more sense to wait and see how the apatite emplacement is performing. If it is performing well, there may be little Sr-90 for the Coyote Willows to take up, i.e. the phytoremediation may be unnecessary. If the apatite emplacement is not working, phytoremediation is unlikely to be an effective back-up.

Proposed Performance Metrics:
Though the only stated metric is analysis of plant material after each harvest, presumably they will also measure Sr-90 in groundwater upgradient and downgradient of the test plot (a better metric).

Summary Evaluation:
Planting Coyote Willows may be an effective polishing technology for Sr-90 contamination at 100-N area. It would be more efficient to understand the effects of the apatite emplacement prior to planting the test plot. If the test plot is planted first and does not perform well, it will be difficult to know why because of the lack of control on individual variables.

Reviewer #3

Target Plume/Area: Strontium-90 Plume – 100-N Columbia River riparian zone, Hanford, WA
Proposal Title: Phytoremediation – Treatability Study along the 100-N riparian Zone

Technical Basis of the Proposal:
The authors propose phyto-technologies as part of a treatment train to remove ^{90}Sr from the soil of the riparian zone and as a filter for groundwater along the Columbia River. In addition to the proposed phyto-technologies, the treatment train consists of an apatite barrier, apatite injection into the vadose zone and monitored natural attenuation. Specific phyto-technologies include phytoextraction and rhizofiltration. The authors propose to use Coyote willow (*Salix exigua*) to extract ^{90}Sr from the soil/groundwater system. Growth chamber studies have shown that various plant species will uptake Sr at various concentrations. Greenhouse studies have shown that Coyote willows will uptake ^{90}Sr and will produce sufficient biomass to remove significant amounts of ^{90}Sr from the system.

The stated objectives of the proposed study are to 1) determine the most efficient fertilization method for the target species that will generate the greatest amount of biomass and be protective of the Columbia River from excess nutrient runoff; and 2) demonstrate the efficacy of using Coyote willow as a "^{90}Sr phytoremediation tool" along the riparian zone associated with the 100-N area of the Hanford Site.

To address these objectives greenhouse studies and test plots will be installed at the site. The test plots will be installed at a location with little or no ^{90}Sr contamination or and area with high ^{90}Sr contamination. The location will be dependent upon funding.

The proposed approach is reasonable and should be an effective approach to evaluate the efficacy of Coyote willow at removing ^{90}Sr by phyhtoextraction and rhizofiltration. Another potential benefit of the study may be identification of best planting techniques (and nuances) to effectively install the vegetation in the rip-rap area. In addition, the study should provide a mechanism to develop and demonstrate appropriate best management practices to be applied at the site to help protect the environment.

Uncertainties associated with this study will be the effectiveness of the willow's rooting system for accomplishing rhizofiltration. Below ground attributes of a plant will be dependent on a number of things and will be hard to evaluate – especially if the initial plantings are placed in the highly ^{90}Sr contaminated areas and are to be left as part of the remediation system. Alternatively a statistically representative sampling of willows should be performed during the study to evaluate the root system of the plants.

Several environmental risks should be managed as part of the study. Specifically, the test plots should be periodically cleaned of leaf litter and small twigs and branches that might fall from the willows. Vector control in the test plots is very important. The vegetation should be protected from rodent activity. For example, during certain times of the year the nutrient rich bark of phreatophytes can be quite a treat for rats and rabbits and other rodents. This is a potential food-chain issue.

One additional risk that should be considered is the potential of fire to damage or destroy the test plots. Appropriate fire prevention measures should be included in the ongoing management of the plots.

Implementation Strategy:

The implementation strategy appears to be appropriate for the objectives of this study. Phyto-technologies are very cost effective to implement. It is unclear if management of the plots (vector control, fire prevention and ongoing cleaning and maintenance of the plot) is included in the budgets. If not these should be added to make sure that it is Because of the nature of the material (contaminated leaves, branches etc) there may need to be special handling and disposal. It is unclear if these costs have been included in the budgets.

Proposed Performance Metrics:

Phyto-technologies together with the apatite sequestration of ^{90}Sr will be a significant improvement of the existing pump and treat system. According to background information, the pump and treat system is not effective in remediating the riparian zone of the Columbia River. The proposed technologies will be effective in reducing the mass of contaminants in the soil and groundwater associated with the 100-N portion of the river.

Summary Evaluation:

In summary, the proposal provides a reasonable approach to remove ^{90}Sr from the system. There are a number of issues relating to the proposal that need to be addressed – specifically, the uncertainties related to the effectiveness of the willows for accomplishing rhizofiltration. Below ground attributes of a plant will be dependent on a number of things and will be hard to evaluate – especially if the initial plantings are placed in the highly ^{90}Sr contaminated areas and are to be left as part of the remediation system. Alternatively a statistically representative sampling of willows should be performed during the study to evaluate the root system of the plants.

Several environmental risks should be managed as part of the study. Specifically, the test plots should be periodically cleaned of leaf litter and small twigs and branches that might fall from the willows. Vector control in the test plots is very important.
The proposal should be funded based on the uncertainties and environmental risks.

Reviewer #4

Target Plume/Area: Sr-90 in the 100N Riparian Zone

Proposal Title: Phytoremediation Treatability study along the 100-N Riparian Zone

Technical Basis of the Proposal:

The technical basis is sound. It is based on uptake studies using the species Salix exigua which is native to the area and is used as erosion control in similar locations. The preliminary work to assess the use of this species was suitable. Use of plants in this circumstance, as a polishing step in conjunction with another method to minimize Sr-90 concentrations in the groundwater upstream appears to me to be very appropriate. This method may provide enough uptake to significantly reduce the quantity of Sr-90 moving through the treated area, by intercepting Sr-90 as it outcrops along the river bank. I doubt if this amount of Sr will make a big reduction in any risk factor but may be useful as PR. Phytoremediation will not be very useful if the upstream method (precipitation of apatite) does not provide substantial retardation of the Sr-90. The main uncertainties revolve around the issue of maintaining a good stand of willow on the site. These plants have been used along the banks of the river, what is the experience with their survival? Examination of existing stands would be useful, and perhaps one of these could be used as a test bed for harvesting and minimizing loss of contaminated material. Apparently the plants can withstand flood events and daily and seasonally high and low water that varies +/- 8 feet. How can fertilizer be applied appropriately? How long is the dormancy period and how much Sr-90 will be lost during this time? If the agronomic issues are overcome then the project seems reasonable and practical. The only alternatives seem to be PRBs and low flow rate extraction wells. Apparently a PRB or mixing zeolite into the soil to enhance Kds is not possible due to the difficult material conditions (gravel and cobbles). It needs to be recognized that this method, as stated in the proposal, is only a polishing step and will extract only a very small fraction of Sr-90. This fraction however is in the most sensitive area in that it is seeping into the river and so I think it is worth trying if all of the stakeholders agree.

Implementation Strategy:

Coupling the phytoremediation activities with the apatite precipitation is useful only if the timing of the injections of solutions to generate the apatite will result in the pulse of elevated Sr-90 in the groundwater passing through the phytoremediation area when the plants are active. It is unclear how long this pulse will be and if the timing can be suitably determined. The last sampling is in March of 2008, should it not be a few months later. Costs for the phytoremediation activities seem appropriate.

In the Budget item #30, the question is raised about if an uncontaminated site should be used. It is pointless to do anything at an uncontaminated site other than a preliminary test to ascertain plant growth. This however seems to be unnecessary since the plants are used in similar environments for erosion control.

After the apatite injections the nature of the groundwater may change in some unpredicted way. While Sr-90 should decrease, after an initial increase due to desorption as a result of the introduced elevated ionic-strength solution, other water parameters may change and influence plant growth?

Proposed Performance Metrics:
This project, especially as it is coupled to the apatite precipitation work, is better than the baseline. We have not been given any estimates of mass balances of Sr-90 currently entering the river along the treated area versus entering from deeper locations that will not be reached by the treatment, but at face value it seems that some contaminant will be stopped from entering the river. This calculation should be done. I think the sampling plan as outlined should be OK. Are the concentrations such that one could track concentrations in the river up-stream and down-stream of the site over time?

Summary Evaluation:
Overall I think this project will provide some benefit by polishing Sr-90 from groundwater outcropping along the river bank. As part of a larger strategy, I think this approach is interesting, appropriate, and has the potential to reduce the input of some Sr-90 into the river. There seem to be few alternatives.

Reviewer #5

Target Plume/Area: 100 N Area

Proposal Title: Phytoremediation

Technical Basis of the Proposal:

1. The project is based on appropriate and valid science; phytoremediation is proven to concentrate various elements based upon the species selected and the conditions under which it is grown. The actual performance of the technology has uncertainty regarding the mass of Sr to be removed over a distinct period of time. In addition, there are some concerns regarding potential impacts on the environment related to implementation of this technology.
2. The likelihood of the desired outcome is fair (but what is the goal, exit strategy?); estimates of time to attain the goal may be overly optimistic (removal rates would have a tail like a pump and treat system).
3. This is a good systems approach, especially given the poor access along the river bank.
4. Approach is reasonable and practicable; costs for this technology are relatively inexpensive.
5. Key risks and uncertainties are related to the overall performance (how much Sr will be removed?) and time required to meet the goal; there is some concern regarding mobilization of Sr due to addition of citrate and apatite solution in a "sistern" project. This other project will add Ca to the system and so the Sr uptake by the coyote willow will likely be less; there is concern regarding addition of fertilizer, which could migrate to the river and may not be necessary, as there already is nitrate and apatite solution adds phosphate. Purpose of the study says it's to investigate fertilization, but should be broader goal, because fertilization may not be necessary.
6. I recommend implementing the apatite barrier (especially the surface infiltration) first and monitoring its performance before phytoremediation is implemented. Based upon the results of the apatite barrier, it may not be necessary to utilize the phytoremediation, as it may not remove significant Sr from the system. Another alternative might be zeolite or apatite soil mixing, but implementation could be difficult.
7. This technology was previously recommended by the ITRC as one tool in the toolbox.
8. Phytoremediation may be impacted by the apatite barrier system; citrate, calcium, etc.; collateral damage is possible. There is definitely concern regarding distribution of Sr in leaves, etc.

Implementation Strategy:

- The sequence and timing of activities may not be appropriate. I recommend sequencing the apatite barrier prior to the phytoremediation.
- The technology can be implemented relatively cost effectively when compared to other alternatives, but the costs estimated may grossly underestimate the costs.
- Good public relations to install this system, but may not remove significant Sr. Hanford needs to be careful about over-promising the performance of a particular technology.

Proposed Performance Metrics:

- The project represents an improvement compared to the current baseline of pump and treat upgradient, as it directly addresses Sr contamination at the river, but may not be significant.
- The project makes an attempt to quickly protect the Columbia River.
- Performance of the technology will be measured as the willows are harvested, but what is the endpoint goal? This should be established prior to implementation.
- Monitoring of water quality at the river's edge will continue and will demonstrate effectiveness of the technology. So there are measurable parameters, but no endpoint goal has been set.

Summary Evaluation:

Overall, recommend this technology as part of the systems approach for the 100-N Area, but may not contribute significantly to the cleanup of this plume. Control of biomass and linkage to the food chain are issues that need to be explained to the stakeholders. Don't over-promise the technology. Develop quantifiable endpoints before implementation.

Reviewer #6

Target Plume/Area: 100N Area

Proposal Title: Phytoremediation - Treatability Study along the 100-N Riparian Zone

Technical Basis of the Proposal:

Is the project or activity based on appropriate and valid science?

Studies of Sr-90 uptake by peach-leaf willow (*Salix amygdaloides*) and cottonwood (*Populus deltoids*) indicated that both species removed Sr-90 from the soil and soil pore water, and under appropriate conditions, might prove effective in the remediation of Sr-90 contaminated soils in the riparian zones of the 100N area. FY 2004 studies examined the ability of the native perennial species coyote willow (*Salix exigua*) to remediate ^{90}Sr contaminated soil, indicating an uptake of 0.39 nCi/g dry weight. Further, estimate of worker exposure during harvesting and packaging of Coyote willow suggested little external dose associated with this activity. The internal dose was estimated at very low levels (2.153×10^{-8} Sv).

What is the technical likelihood of the stated-desired outcome?

Good, based on greenhouse and test plot studies to date. Specific concerns for stated tasks follow:

Task 2: Treatability test – experimental design and engineering (FY 2006 – duration 5 months). How will this test design be "statistically rigorous both on the site selected (physical dimensions available) and the plant variables to be tested (plant density, fertility etc.)." This needs significant explanation. Further, what engineering controls will be in place for the test site? This needs to be explicitly identified. Last, perhaps engineering controls can be tested on a separate, uncontaminated plot (perhaps an existing willow stand?).

Task 3: Fertilization Effects - (FY 2006: duration – 6 months). Need to detail the specifics of the planned studies for fertilizer application rate, timing, and frequency. Besides application rate and time, what other methods may be used/investigated to assist in the control of fertilizer runoff into the Columbia River (how is this communicated this to stakeholders ?

Task 4: Field Treatability Study – Data Collection (FY 2006 thru FY 2008). How will performance be assessed? Assessment in terms of biomass produced, Sr-90 removed? How will variabilities in harvests be addressed? Will other plants that grow in the fertilized test area be examined/evaluated?

Task 5: Data Analysis and Reporting (FY 2006 thru FY 2008). Understand general schedule for plant and water sampling analyses, but how will this data be used to assist in subsequent year's growth/harvest/fertilization activities?

How does the project fit in with the totality of proposed activities for the target contaminant/plume?

The use of phytoremediation/rhizofiltration at the 100-N area is part of a treatment train that includes Monitored Natural Attenuation (MNA), and an apatite barrier. Phytoremediation/rhizofiltration would act as an immediate interceptor of aqueous ^{90}Sr currently within the riparian zone's pore water and a longer term extractor of ^{90}Sr currently sorbed to the riparian zone's vadose and aquifer sediment. In addition, project is widely supported by both state of Washington, but with some concerns from federal (U.S. EPA) regulators, and explicit concern from tribal groups.

Is the proposed approach reasonable and practicable?
Yes.

What are the risks or key uncertainties in the proposed action(s)?
Risks/uncertainties include: (i) development of healthy, growing coyote willows in area of Sr-90 discharge (ensure successful interception of increased Sr-90 plume expected from surface apatite solution injection/infiltration; (ii) protection of coyote willow (*Salix exigua*) plants from potential receptors; (iii) leaching of excessive nutrients (fertilizers) used to enhance plant growth; (iv) ability to ensure harvest/removal of plants prior to high water levels in late spring/early summer, and before winter senescence; (v) inability of phytoremediation to actively remove Sr-90 during non-growth periods (winter); (vi) success of infiltration apatite barrier; and (vii) ensure proper transport and disposal of harvested plants to proper disposal facility.
.
Are there clear examples of alternative ideas or proposals that should be considered?
There are no additional ideas that can successfully target the Sr-90 currently within the riparian zone area without the use of extensive, highly-engineered approaches. Although, given the reasonable acceptance of Sr-90 sequestration with apatite, could the stakeholders now be more receptive to use of xeolite as a barrier trench.

Implementation Strategy:
Is the sequence and timing of activities appropriate?
Yes.

Can the technology be implemented cost-effectively?
Yes. Successful demonstration of growth, protection, and harvest of coyote willow will lead to improved means to remove Sr-90 from riparian zones, leading to improved cost-effective strategy for removal from near shore areas relative to much more extensive engineering approaches.

Is the budget and level of effort appropriate for the proposed work?
Yes, budget and time frame appear reasonable for the stated scope of work (both uncontaminated and highly contaminated areas).

Proposed Performance Metrics:
Does the proposed project or activity represent a significant improvement compared to the baseline?
Yes, as there is no active phytoremediation program to enhance removal of Sr-90 along the riparian zones.

Does the project improve the protection of the Columbia River now or in the future?
Yes.

Are there measurable parameters that would document performance?
Yes. Harvesting of cultivated coyote willows will yield measurable amounts of Sr-90 removal from the riparian zones along the Columbia River. However, study would likely benefit from exploration of both non-contaminated area of 100N in first year to demonstrate feasibility and success of engineering controls; given success, follow in subsequent years by exploration in contaminated area.

Are these included in the proposal?
Not in sufficient detail. For example, data analysis and reporting is very vague in the manner in which the data will be analyzed (e.g., "statistically rigorous"). Specific details are noted above.

Summary Evaluation:

Good proposal that can have very near future impact on removal of Sr-90 from riparian zones of 100N area. Largest concerns are the lack of active phytoremediation during winter (non growth periods), where this polishing step will not be active and concern for influence of apatite solution affecting plants. Further, study should explore both non-contaminated area of 100N in first year to demonstrate feasibility and success of engineering controls; given success, should be followed in subsequent years by exploration in contaminated area.

Reviewer #7

Target Plume/Area: Sr / 100 N Area

Proposal Title: Phytoremediation – Treatability Study along the 100-N Riparian Zone

Technical Basis of the Proposal:
General

- This project is generally consistent with previous peer reviews and recommendations.

ITRD Technology Evaluation
100-NR-2 Operable Unit

Technology	Conclusion	Recommendation
Monitored Natural Attenuation (MNA)	May be appropriate for portion of plume far from the river, but will not limit current discharges of ^{90}Sr from N-Springs.	Should be examined in more detail when establishing Long-Term Stewardship protocols.
Soil Flushing	Likely to be effective in removing ^{90}Sr in the shortest time frame.	Should be examined in more detail with regulators.
Phytoremediation	May be the best option for controlling current releases at the river; leaf litter control may be an issue.	Needs more analysis.
^{90}Sr stabilization by phosphate injection	Design studies were insufficient to support recommendation of the option.	Re-examine this option after the Tanks Focus Area work is completed.
Barrier technologies (clinoptilolite and sheet pile/cryogenic)	Installation is considered feasible. Bank is stable and erosion potential associated with construction is considered negligible.	Precautions during construction should minimize potential damage.

- The proposal is positioned as “linked” to upgradient stabilization (otherwise active phyto-management would need to continue for a much longer time period). This linkage is a strength.

- The technical basis of the action (target levels and end-point criteria) is missing (see performance measures below). This is important because the plants generally remove Sr in the water (circa 1% of the inventory) but only indirectly from the soil (circa 99%) of the inventory. Thus, the statement that studies have “demonstrated the ability of phytoextraction to remove ^{90}Sr from soil/water” may be optimistic. The proposal goes on to state that the expected treatment period is 7 to 30 years, but there is little basis for this. Another impact of this issue is that there is no technical basis for identifying where to do the phytoextraction (What ^{90}Sr activities justify the action? When are ^{90}Sr activities too low to justify the action?) This topic is significant and I recommend that the proposers develop a technical basis for setting action and endpoint levels and that these be examined in the treatability study to determine a more realistic idea of cost and timeframe.

- Collateral Impacts - The potential for real or perceived biological “release” via plant litter and fauna migration is a significant issue. The nature of such biomass and migratory release from

Coyote Willow ecosystems should be considered by the researchers and estimated – this should be explored with stakeholders to determine acceptability criteria. If Herculean steps are needed to avoid this release pathway for the extraction to be accepted, then this technology is unlikely to be a clear success. Alternatively, if the researchers can document performance in terms of projected reductions on flux to the river ecosystem and possibly put passive litter collection downstream then this may be promising when combined with the upgradient insitu stabilization.

- Would apatite sequestration at low water stage be an alternative treatment concept?

- May be difficult to implement in a comprehensive manner in the presence of large surface rip-rap.

- Two alternatives are proposed (a nonrad site and a rad site). The nonrad option would not provide the data needed to address several of the issues and hypotheses. Notably, if done at a nonrad site the linkage to the apatite injection and the plants as a near-time protection to avoid flushing Sr to the river would be negated.

Specific

Page 2 –
No clear basis for the 5 to 30 years is presented in the proposal or background material.

Page 3 –
Good discussion/presentation of the appropriateness of a "combination" of technologies. Good explanation of why Coyote Willow.
Repeat 5 to 30 year projection without basis.

Page 4 –
Proposal states that phyto will only be needed for 5-7 years if done in combination with apatite. No basis presented and this may be optimistic since the bulk of the contaminant is sorbed. Good linkage of phyto to stabilization however.

Page 6 –
Estimated Uptake may be optimistic and was not demonstrated in initial tests but was inferred by adjusting uptakes for expected higher growth rates.
Worker exposure discussion is good.

Page8 –
Costs for research are generally reasonable but the overall cost for up to 30 years of deployment appear too low (see performance metrics).

Page 10 –
Foliar application of nutrients may be a good idea as proposed but is labor intensive.

Implementation Strategy:
Schedule is generally reasonable and provides several (about 4) biomass harvests. Note that nonrad site alternative may not be as useful as rad site alternative.

Proposed Performance Metrics:
Need to provide the technical basis for application (limits and ending criteria). These need to be examined in the treatability study.

Lifecycle costs do not appear consistent – research for 2 years is 700K and the entire 30 year estimate is 1600K. If the lifecycle costs do not include the 700K then the approximate cost (not accounting for time value of money) is about 60K/year! This seems low for labor to fertilize, harvest twice and dispose of 10-12 metric tons per hectare to the low level disposal site. If the lifecycle costs include the 700K then the last 28 years are about 900K or less than 35K/yr!

Summary Evaluation:
Good proposal. Need to address:

Technical basis of the action and projections of timeframe.
Collateral impacts.
Alternative of apatite application during low water stage?
Check and make sure lifecycle costs are realistic.

Reviewer #8

Target Plume/Area: 100-N Riparian Zone

Proposal Title: *Phytoremediation – Treatability Study along the 100-N Riparian Zone*

Technical Basis of the Proposal:

Is the project or activity based on appropriate and valid science? Phytoremediation can under certain conditions provide a valid method for site remediation. This proposal indicates that phytoremediation will be effective for removing Sr from the vadose soils and act as a filter for ^{90}Sr released as a result of the upgradient infiltration of the Ca-Citrate-PO_4 solution. Typically removal of contaminants from the soil will occur over a period decades but can be a valid approach when other more aggressive removal strategies are not practical. This reviewer believes that it is not likely to be a valid approach for filtering ground water based on ground water flux and willow water use efficiency (see discussion below).

What is the technical likelihood of the stated-desired outcome? The two primary stated outcomes are 1) determination of the most efficient fertilization method, and 2) demonstration of the efficacy of using Coyote Willow as a ^{90}Sr phytoremediation tool.

It is unclear from the proposal if the need for fertilization given planned phosphate injection and current ground water chemistry in the area is required. It is therefore unclear if the greenhouse studies will significantly add to this program.

It is more likely that the present proposal will provide information on the potential efficacy of using phytoremediation to remove ^{90}Sr from the vadose zone within the riparian zone.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? It is suggested that the proposed activities fit in synergistically with the other planned activities (i.e. phosphate infiltration) due to:

1. Microbial ecology associated with rhizosphere,
2. Rhizosphere will act as filter for plug-flow displaced ^{90}Sr from ground water,
3. Apatite will sequester most of the rest of Sr (thereby decreasing time for phyto, and
4. Willows will act as bio-monitors for apatite efficacy

In response to these potential synergistic outcomes,

- The addition of Ca-citrate during the proposed apatite infiltration approach will provide abundant nutrient to stimulate microbial growth, and in fact for success, the process requires that the indigenous microbial population will break down the citrate thereby making available Ca for the precipitation of apatite.

- It is unlikely given the flux of ground water to the Columbia River and the water use efficiency of willows that filtration will have a significant impact of the transport of Sr to the river. Quick calculations of water use efficiency (WUE) indicate that 0.9 ha of willows (*Salix goodingii*) could only extract about 8% of the ground water passing the 300 m long phytoremediation zone. This calculation assumes biomass production of 12 MT/acre, a WUE of 540 g H_2O/g DM, a saturated thickness of 15 m, a porosity of 35%, and a ground water velocity of 0.3 m/d. These calculations should be checked with possible better site-specific assumptions.

- Given the likely sequestration of ^{90}Sr by apatite, it is unclear why this technology should not be expanded to the riparian zone thereby eliminating the need for a supplemental remedial technology (e.g. phytoremediation) and bypassing the potential ecological risks associated with the phytoremediation.

- Given the proposed monitoring that would be done in conjunction with the phosphate infiltration technology, it is unclear how bio-monitoring would provide much additional valuable information.

<u>Is the proposed approach reasonable and practicable</u>? It is unclear to this reviewer that evaluating a fertilization regimen (Task 3) is practical or reasonable in lieu of the site conditions. Field treatability studies (Task 4) should provide some evidence for site-specific Sr uptake effectiveness. However, conducting the field studies in an uncontaminated area would appear to provide little useful data and therefore if the project moves ahead only field studies in the contaminated region would seem to offer significant useful information.

<u>What are the risks or key uncertainties in the proposed action(s)</u>? The most obvious risk is the transfer of ^{90}Sr from the current soil/ground water reservoir to the plant reservoir which potentially alters the bioavailability and ecological receptors.

<u>Are there clear examples of alternative ideas or proposals that should be considered</u>? The injection and infiltration of Ca-citrate-PO_4 solution alone with the exclusion of the phytoremediation component.

Implementation Strategy:

<u>Is the sequence and timing of activities appropriate</u>? The proposed schedule for this project would have field studies beginning in 2006, significantly ahead of the phosphate infiltration field tests. It is likely that the infiltration of large quantities of phosphate, depending on the degree of transport could significantly affect/alter site-specific conditions and therefore it would seem that conducting this type of testing in conjunction with apatite testing would be appropriate. In addition, it may be prudent to evaluate the success of the apatite injection program to determine if the phytoremediation component will be required.

<u>Can the technology be implemented cost-effectively</u>? This will ultimately depend on the ability of the phytoremediation strategy to significantly affect levels of ^{90}Sr being transported to the Columbia River, and is difficult to assess at this point.

<u>Is the budget and level of effort appropriate for the proposed work</u>? Budgetary analysis is better addressed by those familiar with costs typically associate with this type of work at national labs.

Proposed Performance Metrics:

<u>Does the proposed project or activity represent a significant improvement compared to the baseline</u>? The proposed may be an improvement compared to baseline P&T system, as the current technology does not appear to be controlling release of ^{90}Sr from the riparian zone to the Columbia River. It is unclear to what extent the technology can improve on the currently proposed apatite sequestration technology.

<u>Does the project improve the protection of the Columbia River now or in the future</u>? Should provide some, though modest protection of the river resource.

<u>Are there measurable parameters that would document performance</u>? The experimental design and metrics for evaluating the success of the studies in meeting the stated objectives are not provided in enough detail within the proposal to make this determination.

<u>Are these included in the proposal</u>? (see above)

Summary Evaluation: It is unclear to this reviewer that the phytoremediation component is necessary given the potential of the apatite to sequester ^{90}Sr within the vadose and saturated zones. It would seem prudent to evaluate these technologies prior to implementing an additional technology that may add little additional benefit and may potentially transfer strontium to a more bioavailable reservoir.

APPENDIX C

Refine Location of the Chromium Source at the 100-D Area

Target Plume/Area: Chromium (Cr(VI)) / Hanford 100-D Areas

Proposal Title: Refine Location of the Chromium Source at the 100-D Area

Proposal Reviewers: Dawn Kaback, Todd Anderson, David Cocke, Jeff Daniels, Gene LeBoeuf, David Lesmes, Brian Looney, Louise Pellerin.

Summary Evaluation:
The panel supports the goal of refining the source location of chromium contamination in the Hanford 100-D Area as part of the overall systems approach; however, the panel does not recommend funding the proposal as written. Instead, the panel recommends a new proposal be written to replace this one. The panel does not believe surface geophysics can be used to directly identify the source, but likely has a significant role in furthering understanding about the hydrogeology in the vicinity of the source area.

The panel recommends a two-pronged approach for the problem: 1) investigate a Cr source known to exist at the 100-B Area (yellow soil) and possibly other sources that may be identified during excavation of piping in the 100-D Area in 2006 (i.e., if yellow soil is identified) to enhance understanding of Cr transport, fate, and form in the vadose zone by using geophysical and geochemical methods (possibly using Enhanced Access Penetration System [EAPS] or other direct push technology to install boreholes); 2) if source identification is successful in the 100-B Area, utilize similar methods in the 100-D Area, near suspected sources.

Technical Basis of the Proposal:
The panel believes the proposed use of geophysics is not likely to achieve the desired outcome of directly identifying the chromium source in the 100-D Area. The most important and overarching themes of the panel recommendations are: 1) success of any source identification effort requires a clearer conceptualization of the expected nature and form of chromium in the source; and, 2) supplemental technology solutions should be developed and implemented based on their responsiveness and sensitivity to the expected nature of the source. Refining the conceptual model based on existing data and focused study is a prerequisite to successful source identification. As described below, the peer review panel does not endorse a source identification effort built primarily around geophysics in this setting, nor does the panel endorse an unconstrained brute force drilling and sampling program.

Geophysics will not be the “silver bullet” that directly locates the source of chromium contamination, but geophysics may be useful to enhance understanding of the stratigraphy of the vadose zone and may be able to identify areas or traps where the contamination is likely to exist. In order to effectively use geophysics to identify these traps, a better conceptualization of the

nature of the controlling features and the source zones will be needed. (see reviewers 3,4,5, and 6)
The first step recommended is study of an area of known Cr contamination in the vadose zone to understand transport, fate, and form of Cr. Build a conceptual model for the 100-B Area Cr contamination and then test various geochemical and geophysical methods at this site of known contamination, prior to application of these methods at the 100-D Area. Use an integrated approach with multiple methods to provide "defense in depth." (see reviewers 2,3,4,5,6,7, and 8)

- Geophysical methods should include surface, borehole, and cross-borehole tomography using methods such as radar, seismic, and resistivity. SP measurements do not appear to be promising and have not been proven for this type of application. Geophysics can only be applied with sufficient geologic information to provide ground truthing. Consider adding exploration geochemistry methods if a suitable hypothesis and signal can be identified in the vicinity of the source zone.
- Boreholes will first have to be drilled to obtain geologic samples for chemical (for Cr total, +3, and +6, because the solid form may be Cr+3, which is oxidized to Cr+6 as it dissolves into the pore water) and SEM analyses (map the Cr and validate identification of the form of the Cr) and for ground-truthing the geophysics.
- Past data should be reexamined to determine if there are any important issues associated with extraction efficiency of Cr(VI), if Cr(III) at high concentrations in a source zone may contribute low but stable levels of Cr(VI). A review process, along with the focused study of the 100-B site, would provide information about the potential "signals" expected in the source zone (both geophysical and geochemical) and would help in determining the appropriateness of potential source treatment alternatives.
- Boreholes should be geophysically logged (consider neutron logs and investigate other tools that can be used in cased holes) and install casing for cross-borehole tomography. Radar requires PVC casing, whereas seismic requires steel casing (and boreholes must be filled with water using FLUTe technology).
- After identification of the form and structure of the Cr in 100-B, develop a clear conceptualization and a limited number of hypotheses about the nature of Cr sources in the Hanford setting near the Columbia River. Determine if there are alternative signals that can be identified, such as soil gas or push-pull testing. If so, collect soil gas samples either during drilling of additional boreholes or possibly from shallow sampling. Push-pull testing will require installation of screened vadose-zone monitoring points.

After the work is completed at the 100-B Area, a similar detailed site investigation should be conducted at the 100-D Area near the suspected source areas. This investigation should utilize the methods that were successfully applied at the 100-B Area (described above) and should include data necessary to construct a conceptual model for this location.

- At the 100-D Area, the goal of the site investigation to identify stratigraphic traps for the Cr could be very difficult to demonstrate as the entire section may consist of extremely coarse-grained materials, with sand as the finest grain size present.
- Consider using EAPS to reduce costs. Direct-push technology can provide continuous resistivity information.

- Prior to drilling with EAPS, perform low-frequency ground-penetrating radar (GPR) surveys to locate large boulders that can then be avoided when identifying drill locations, and map cultural interferences that would also impact future geophysical surveys. GPR may be useful for mapping subsurface geology to 30-foot depth.
- In addition to the use of GPR for reconnaissance either prior to other surface geophysical surveys or drilling, use electromagnetic methods (e.g., EM-31), ground conductivity meter (GCM), or magnetic surveys.

Other alternatives that could be considered include:

- Further investigate impact of acidic chromate solutions on chemistry of soil, perhaps looking at uranium and daughter products. Obtain more information about the chemistry of the chromate solutions in terms of potential co-contaminants, pH, etc.
- Consider the use of forensic groundwater/vadose zone modeling to better define the source locations.
- Consider tracer testing to enhance the conceptual model of subsurface migration of contaminants.
- Consider application of induced-neutron gamma ray spectroscopy (e.g., Herron and Herron, 1996) to obtain high-resolution geochemical logs of cased holes. These data can typically be utilized to infer formation lithology and possibly hydrogeological parameters. However, formation lithology data may not be that useful at the 100-D Area, as the entire section will be very similar mineralogically and will contain primarily quartz.

Implementation Strategy:

The proposal calls for convening an expert panel to recommend geophysical methods for direct detection of Cr. This activity is not recommended since it duplicates efforts of a previous panel that stated that geophysics could not be used to directly detect Cr in soils, especially given the current understanding of the geology of the vadose zone. This review panel supports the findings of the earlier panel and recommends that this proposal not be supported as written.

If a new proposal is prepared, it should be peer reviewed, including evaluation of the implementation strategy.

The panel recommends a phased approach, beginning with investigation of a known chromium source area, testing of methods for detection, and later application at the 100-D Area.

The panel also recommends an integrated strategy that involves use of multiple methods, including geophysics and geochemistry to build the conceptual model. “Defense in depth” is required to ensure better success in the face of this challenging problem.

Proposed Performance Metrics:

- Performance metrics are not specifically included in the proposal. A more detailed description of specific performance objectives is needed.
- If a new proposal is prepared, it should be peer reviewed for proposed performance metrics.

- Specific and clear performance metrics must be developed to make this project a success. Better definition of what is a Cr source is desirable.

Reviewer #1

Target Plume/Area: Chromium/Hanford 100-D Area

Proposal Title: Refine Location of the Chromium Source at the 100-D Area

Technical Basis of the Proposal:

Is the project or activity based on appropriate and valid science?

Yes. The potential of geophysical techniques to locate source zones of contamination in the 100-D area needs to be verified. Geophysical techniques have great potential for use in determining the location of source zones of contamination without the need for expensive exploratory drilling. However, these techniques still require testing and validation in the field and this proposal will examine several techniques at the 100-D Area.

What is the technical likelihood of the stated-desired outcome?

The proposal will examine several geophysical techniques for use at the Hanford 100 Area. The results will be determined during these field tests.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable?

The project addresses finding the location of the source zones of Cr contamination for aggressive source treatment. This is a high priority activity and an integral part, if not one of the most important parts, of the overall "systems" approach to site remediation at the 100-D area. If it is not possible to the detect source zones of low or intermediate contamination the geophysical measurements will still provide extremely valuable information on the hydrologic properties of the subsurface.

What are the risks or key uncertainties in the proposed action(s)?

There are no risks associated with examining the use of geophysical techniques to locate source zones in the 100-D area. However, if the geophysical techniques prove to be not useful in identifying source areas then the fallback position for finding these sources is exploratory drilling along inferred/suspected Cr contamination pathways. The fallback position is expensive. The lure of substantial cost savings by using/validating the use of geophysical techniques to find these source zones is too great to ignore and should be examined.

Are there clear examples of alternative ideas or proposals that should be considered?

If no geophysical methods can be validated in the field for finding source zones then the fallback position is exploratory drilling/excavation. This is expensive. A strong effort should be made to identify and validate appropriate geophysical methods to detect these source zones. The potential cost saving are too large to ignore. However is this an activity better pursued by other elements of DOE, such as Office of Science?

Implementation Strategy:
Field-testing of various geophysical techniques should begin as soon as possible.

Proposed Performance Metrics:
No single detection method should be relied on exclusively to detect source zones within the 100-D area and geophysical techniques are no exception. Ultimately the detection of suspected source zones by geophysical methods needs to be verified by examining the local groundwater chemistry, analysis of subsurface samples and even historical operations records for past activities in the given area. Bottom-line…the geophysical results need to be interpreted in the context of the conditions found at the site. These techniques are but one tool for use by environment managers and should not be used alone as the sole criteria for identifying source zones.

Summary Evaluation:
The examination of geophysical techniques to identify source zones of Cr contamination has the potential for substantially reducing the costs associated with finding these source zones. However, the results of geophysical detection methods for identifying source zones need to be demonstrated to be possible and must be interpreted in the context of other available information in a given area such as local groundwater chemistry, analysis of subsurface samples and even historical operations records for past activities in the given area. I have no objection to the proposed examination of geophysical techniques to detect source zones as long as it is understood that geophysical techniques are but one tool to be used for source zone detection. In the event that geophysical techniques cannot detect source areas (a strong possibility) the added benefits of incorporating these techniques in refining the conceptual model of the site would be invaluable. The panel recommended, as do I, that the proposal be framed in the context of using geophysical techniques to refine the conceptual hydrologic model of the site and aid the overall "systems" approach to remediation in the 100 Area.

Reviewer #2

Target Plume/Area: Hanford Site, 100-D Area

Proposal Title: Refine Location of the Chromium Source at the 100-D Area

Technical Basis of the Proposal:
Is the project or activity based on appropriate and valid science?

The project is not based on valid and appropriate science since it is very unlikely that geophysical techniques can perform the targeted tasks. Geophysical techniques are generally not capable of low-level chemical contamination location. The main objective of the proposed work is to locate the chromium source feeding the southwestern plume in the 100-D Area using geophysical techniques to indirectly locate either the proximal portion of the groundwater plume or a chromium source in the vadose zone. The first task to determine the appropriate and valid science by convening a panel of experts in electromagnetic geophysical methods to determine which technology(s) would be appropriate to accomplish the objective is questionable. The two remediation techniques being considered: infiltration of a liquid reductant (e.g., calcium polysulfide) or infusion of a strongly reducing gas (e.g., hydrogen sulfide) have both been successfully tested and/or deployed for remediating hexavalent chromium in the vadose zone, so the appropriateness an validity of the science is here is assured.

Geophysical methods can help identify the presence or potential for preferential transport pathways or Cr(VI) possible accumulation sites; help assess the effectiveness of contaminant isolation systems; help identify and support alternative conceptual flow and transport models (particularly trajectory backflow approaches and help the decision-makers through communication of the monitoring data using three dimensional data correlation, analysis and visualization techniques. These need to be considered as more valuable than the location of the Cr source since geophysical methods can only give likely locations but not exact locations.

What is the technical likelihood of the stated-desired outcome?

There is little technical likelihood of the stated-desired outcome as evidenced by the numerous methods of source location being considered and none seem to be one that might be the most appropriate one. Again, the geophysical methods capabilities need to be carefully considered even before any panel of experts would be convened.

How does the project fit in with the totality of proposed activities for the target contaminant/plume?

The application of geophysical methods to determine the location of the Cr source is not appropriate. The best application of the three remediation methods being proposed would occur if the sources(s) can be detailed but it is doubtful if geophysical methods can provide information on refinement of the source location other that identify most likely locations. CPS, EC and ZVI would all be improved by knowing the location of the most concentrated Cr source. However, source location fits well with the totality of the proposed activities for the target chromium and the plume(s) identified in the 100 D area. The refinement of the location of the Chromium Source in the 100 Areas would be a great first step for the application of the treatment and remediation technologies. It will allow a more directed application of both CPS and EC. However, the proposers should rethink the proposed approach using geophysical methods alone.

Is the proposed approach reasonable and practicable?

The new, integrated approach to accelerate cleanup of chromium in the 100 Areas is absolutely the most reasonable and practicable approach. The integrated approach of detailed location of the Cr source and then using an insitu reductant, building more robustness in the ISRM's and using a chemically complementary technology of EC is excellent. However, geophysical methods are unlikely to work and so these are not appropriate as proposed.

What are the risks or key uncertainties in the proposed action(s)?

The risks and uncertainties are associated with the application of the best geophysical methods to determine the location of the source(s) of Cr. This will probably not result in the location of the Cr source(s) and would then discourage appropriate use of the geophysical methods.

Are there clear examples of alternative ideas or proposals that should be considered?

There needs to be some very innovative thinking to develop some alternative ideas such as back trajectory modeling and correlation of geophysical methods with the treatments that are planned. Other alternatives are outlined in the proposal.

Implementation Strategy:

Proposed Performance Metrics:

Does the proposed project or activity represent a significant improvement compared to the baseline?

Conventional drilling and trenching, coupled with groundwater monitoring and excavation of near-surface waste sites are the baseline.

With the objective of the new integrated approach to significantly shrink the chromium plumes while continuing to protect the ecological receptors and human health at the river, the proposal to locate the plume source(s) would be a significant improvement compared to what is being done and what has been done. The geophysical techniques will not provide a breakthrough in source location but combined with other considerations could help in delineating the problem and solutions.

Does the project improve the protection of the Columbia River now or in the future?

Locating and attacking the high concentration sources of CR will provide added protection to the Columbia River.

Are there measurable parameters that would document performance?

Verification of geophysical information will be accomplished with the use of innovative drilling techniques, the EAPS and a percussion drill, to sample the vadose zone and groundwater.

Are these included in the proposal?

Yes.

Summary Evaluation:

Unfortunately, geophysical methods are not likely to locate the Cr source(s). Convening a panel of experts would have to be done with a complementary group of experts in site ground water remediation including some geophysical experts and others that can help delineate the possible locations of Cr sources, preferred flow paths, geochemical considerations, etc, all combined with the planned physical and chemical treatment of the Cr problem by the systematic approach projected by the Cr remediation proposed in the ZVI, CPS and EC approaches. As currently written, this is not a good approach to delineate the location of Cr sources. The project should be further considered before proceeding.

Reviewer #3

Target Plume/Area: Chromium / Hanford 100-D Area

Proposal Title: Refine Location of the Chromium Source at the 100-D Area

Technical Basis of the Proposal:
The overall systems approach taken in the 100-D and 100-K areas as defined in the proposal appears to be excellent, with the exception of the geophysical approach for locating the source(see below). I am not qualified to comment on immobilizing the mass in the ISRM plume with calcium polysulfide, the probability of mending the ISRM barrier by injecting micron-sized zero valent iron, or the use of the electrocoagulation treatment system: This I leave to the geochemists and engineers to evaluate. The remediation approach in the 100-K region appears to be fairly routine stuff, which tells me that the engineers have this problem well in-hand. The overall systems approach to solving this problem is the most likely route to a successful conclusion. The use of tracer tests coupled with borehole measurements is highly recommended.

The impediment to a long term-solution to remediation is heterogeneity of the vadose zone materials, as these materials can interfere with any remediation methods. Detailed characterization will require a phased combination of drilling and sampling of materials, along with the development of a conceptual model of the geology and vadose zone hydrology.

Geophysics may be effectively used as an aid to characterizing the geology, but not as a direct detection tool for the chromium. There is no known way to directly detect and map chromium at these low concentration levels. However, surface and borehole (e.g., cross-hole) geophysical measurements should be tied to geophysical measurements (conductivity and/or seismic geophysical well logs) in individual boreholes, or measurements on the tip of a direct push sampling device. Obtaining geophysical well log measurements in the boreholes is a well-known problem at the site, particularly in holes with stainless steel casing. I am sure that a wide variety of approaches have been used at the site in attempts to obtain geophysical well logs, but in the case of electrical measurements, I suggest trying to use side-wiping sponge electrodes inside a perforated PVC or fiberglass casing. I have used this method successfully under similar conditions (volcanics) at the Nevada Test Site.

The geophysical methods of choice at the site are resistivity (ERT), possibly seismic (if, and only if, good signals can be transmitted and received in the vadose zone), and GPR to define the distribution of near-surface pipes and other buried features. If the penetration depth is adequate using low frequency antennas, then GPR might also prove useful for defining geologic features in the vadose zone.

The SP measurement tests do not appear promising, and there are many fundamental questions associated with the use of SP even under the best of conditions. I am not convinced that there is anything special about the HRR measurements over conventional resistivity measurements displayed in 3D. The HRR measurements could be used as a mapping tool, but it is very unlikely that they can help with the source definition problem any better than any other electrical resistivity method.

Implementation Strategy:
Overall, the proposed implementation strategy for the general drilling, sampling, and geochemical remediation is very good. However, a key to the success of the remediation will be the successful mapping and characterization of the near surface geology should be an integral part of the remediation strategy. And, the geologic and hydrologic information should be tied together through the development of a three-dimensional conceptual model of the site. The model should be established and modified as more information is obtained.

Proposed Performance Metrics:
The overall primary performance metric will be the amount of contaminant measured in monitoring wells. This will be the only true metric for the geochemical and engineered remediation strategies.

The performance metrics for the individual measurements along the way (e.g., geophysical measurements) will be how they fit with the hydrologic and geologic information obtained from the wells, and ultimately the measurement of contaminants.

Summary Evaluation:
Overall, the systems approach proposed is very good. However, I do not recommend the use of geophysics as a means to directly detect the chromium plume, or to define the source. I do recommend the use of geophysics (resistivity, GPR, and possibly seismic reflection) to help define the geologic framework and to bridge the information between boreholes. Obtaining electrical and seismic geophysical well logs will be key to the successful interpretation of geophysical data at the site.

The systems approach for remediation should be tied to a phased exploration approach to define the hydrology and geology, and all of these data should be integrated into a 3D conceptual model that evolves as more information is obtained in the field.

Reviewer #4

Target Plume/Area: 100 Area

Proposal Title: Refine Location of the Chromium Source at the 100-D Area

Technical Basis of the Proposal:

1. The project, as currently scoped, is not based on appropriate and valid science.
2. The likelihood of the desired outcome is very poor; the challenge of directly detecting parts per million of chromate in the subsurface is probably too great. We however, recommend a systems approach that begins with better definition of the geology to target locations for borehole installation. This systems approach could include application of surface geophysics to search for permeability barriers that might have acted as traps for the source material. Further definition could be accomplished using geophysics in cross borehole, downhole logging, or surface to borehole mode. Boreholes should be cased with PVC to accommodate various types of geophysics, such as radar and resistivity; seismic can use steel casing. Additional tests that might include geochemical approaches, such as tracer tests, soil gas, etc. should be considered. We need a better understanding of how the Cr moved into the vadose zone and where it might be trapped. I recommend doing a thorough field investigation at the 100-B Area site where chrome is present in the shallow subsurface (yellow soil). Do an analysis of form of Cr, location of Cr in vadose zone, and then try the exploration methods that may use geophysics or geochemical methods. If the methods are successful at 100-B, they can later be applied at the 100-D Area.
3. Approach is not practicable.
4. Were other alternatives examined? Not aware of other alternatives examined?

Implementation Strategy:
(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work? <u>If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)</u>

1. No discussion of implementation as project is not recommended as scoped.

Proposed Performance Metrics:
(Does the proposed project or activity represent a significant improvement compared to the baseline? Does the project improve the protection of the Columbia River now or in the future? Are there measurable parameters that would document performance? Are these included in the proposal?)

1. The project has potential to significantly improve conditions in the 100-D Area if it could be accomplished; however, likelihood of success is nonexistent as currently scoped.
2. The project attempts to protect the Columbia River in the near term.

Summary Evaluation:
Project is NOT recommended as scoped. I don't recommend another expert panel.
I recommend a geological investigation in the 100-D Area using EAPS to better understand subsurface stratigraphy as well as an investigation of the form and transport of Cr in the 100-B area. After investigating a location where a chromium source is known to occur and applying various investigation methods such as geophysics or geochemistry at a known site, the technology can then be applied at the 100-D Area. Be sure to investigate the 100-B Area site for the form of the chromium. It might be possible that it is present as Cr+3 in addition to Cr+6? May also look for Cr form and location near pipelines being excavated in 100-D Area in the near future.

Reviewer #5

Target Plume/Area: 100D Area

Proposal Title: Refine Location of the Chromium Source at the 100D Area

Technical Basis of the Proposal:
Is the project or activity based on appropriate and valid science?
Maybe. Commonly employed geophysical techniques are based on sound science. The major objective of this effort is to utilize geophysical techniques to indirectly locate either the proximal portion of the groundwater plume or a chromium source in the vadose zone in the 100D Area. This information will be used to remediate the sources, which will also accelerate cleanup and lead to a final ROD.

What is the technical likelihood of the stated-desired outcome? Fair. Highly dependent on method employed, and significant challenges remain regarding detection of chromium (not very conductive metal). One is thoroughly characterizing groundwater at the head of the plume, using conventional or innovative drilling techniques (such as the Enhanced Access Penetration System (EAPS)) to identify the most concentrated and/or furthest upgradient portion of the groundwater plume

How does the project fit in with the totality of proposed activities for the target contaminant/plume? This effort represents an integral component of an overall systems-based approach to remediate the chromium plume in the 100D area. Specifically, this effort is geared towards indirectly locating either the proximal portion of the southwestern groundwater plume or a chromium source in the vadose zone using geophysical techniques. Additional projects include (i) reinforcing (or repairing to some degree) an existing insitu redox manipulation (ISRM) barrier placed in the 100D area in 1999; (ii) immobilization of chromium in the ISRM plume by circulating a strong reductant, calcium polysulfide, in the aquifer; (iii) enhancing the current pump and treat effort by replacing the ion exchange treatment method with electrocoagulation; and (iv) remediation of waste sites along the Columbia by 2012 through the River Corridor. This suite of proposed activities is oriented towards generating a reduction environment. While good, this proposal and each of the other three chromium-plume related proposals, would greatly benefit from direct comparison with alternative methods regarding technical feasibility and especially cost.

Is the proposed approach reasonable and practicable?
Yes, although this reviewer has significant concern with the lack of detail and statement of performance objectives in this proposed effort.

What are the risks or key uncertainties in the proposed action(s)?
Risks/uncertainties primarily relate to the ability of the selected geophysical method(s) to locate the chromium source in the saturated zone and/or the vadose zone. From a systems approach to tackling this problem, this reviewer envisions the use of geophysics in combination with geochemistry, geology, and hydrology, as a means to assist in (i) further refining source zone

location; (ii) further refining geologic and hydrologic conceptual model of the area that can assist in remediation activities (i.e., improved understanding of insitu redox manipulation (ISRM) barrier; best location for additional application of reduction technologies (e.g., calcium polysulfide) to benefit use of "defense in-depth" techniques).

Are there clear examples of alternative ideas or proposals that should be considered?
Yes. Enhanced Access Penetration System (EPS), and use of existing plume and geology information coupled with forensic modeling.

Implementation Strategy:
Is the sequence and timing of activities appropriate?
Yes, although additional "preliminary" effort should be made to make use of existing plume and geology information coupled with forensic modeling.

Can the technology be implemented cost-effectively?
Maybe. Geophysical techniques can be fairly inexpensive relative to numerous bore holes and soil/groundwater sampling.

Is the budget and level of effort appropriate for the proposed work?
No. Lack of sufficient detail on budgeted items (e.g., $300k for geophysical work – what does this work constitute?; and $500k for EAPS, which may or may not be employed).

Proposed Performance Metrics:
Does the proposed project or activity represent a significant improvement compared to the baseline?
Yes. The current baseline technology employed conventional drilling and trenching, coupled with groundwater monitoring and excavation of near-surface waste sites.
Use of geophysical techniques (and/or EAPS) coupled with appropriate modeling may greatly enhance the ability to locate the source of the chromium plume.

Does the project improve the protection of the Columbia River now or in the future?
Yes, success of this effort (i.e., location of the source plumes) can significantly reduce the time, expense, and potential for migration of the chromium plume to the Columbia River in the future.

Are there measurable parameters that would document performance? Not specifically stated in the proposal. Stated performance objectives should include: (i) criteria for selection of geophysics "expert" panel; (ii) performance matrix to guide decision of panel on method selection (what will they evaluate? Cost, performance, reliability, combinations of the above?); (iii) clear articulation of what defines "success" of a method reliably detect chromium plume in vadose zone/saturated zone (further, will these methods be evaluated at or near the vicinity of known locations of chromium contamination (in the vadose zone and in the saturated zone)? (iv) decision support to identify when alternative methods (e.g., EAPS) will be employed (and related performance measures for that method).

Are these included in the proposal?
No – at least not in sufficient detail to discriminate success for failure.

Summary Evaluation:
In general, the ideas put forward with this proposal are good relative towards achieving accelerated reduction of contaminant plume in the 100D Area. Strengths include (i) targeting the sources of the chromium plume(s); (ii) employment of relatively inexpensive geophysical techniques; (iii) potential use of tracer studies, coupled with geophysical techniques, to further identify velocity and direction of groundwater flow, and the further coupling of this information as constraints within a backward-in-time modeling effort to provide estimates of source locations. Concerns include (i) lack of sufficient detail/technical support (i.e., literature support) for potential methods of employment (including modeling tools) – much too open ended regarding potential methods (where is the decision support flow? (also see comment (v) below)); suggestion of combining both geophysical techniques to better locate (and log) new wells lined with polyvinyl chloride to better understand vertical stratigraphy in this particular area; (ii) complete lack of proposal detail on use of conventional or innovative drilling techniques (i.e., Enhanced Access Penetration System (EAPS)) (the “second indirect method”) to identify the most concentrated and/or furthest upgradient portion of the groundwater plume. The proposal notes that the focus is on use of geophysical techniques, yet almost 60% of the budget is devoted to EAPS. Either EAPS and the associated budget amounts should be removed, or the proposal scope should be expanded to include the justification/plan for employment of EAPS; (iii) has not the available plume information already been coupled with backward-in-time modeling to provide estimates of backward location and travel time probability distributions for the observed contamination? If so, what are these results, and how can they be incorporated in this study? If not, why not? (iv) little to no detail on performance metrics (e.g., what criteria will be employed to guide the selection of the panel of geophysics “experts”?); what will define failure or success for geophysical techniques; when/how can employment of EAPS be justified?

Reviewer #6

Target Plume/Area: Chromium Plume/ 100-D Area

Proposal Title: Chromium Source at the 100-D Area

Technical Basis of the Proposal:
The general idea of using geophysical methods to help characterize the subsurface structure and hopefully refine the location of the chromium sources at the 100-D Area is appropriate and reasonable. Geophysical methods can also be extremely useful for monitoring the proposed Calcium Polysulfide injections that will be used to accelerate the reduction of Chromium VI at the 100-D Area and perhaps for assessing the effectiveness of the planned repairs to the deteriorating portions of the ISRM. Comprehensive geophysical logging in all of the available wells should also be a key part of the subsurface characterization at the site. If the geophysical studies are well planned and well executed it is likely that they will greatly enhance the overall objectives of the “systems approach” to cleaning up the 100-D Area.

The proposed plan, however, of using some yet-to-be-determined geophysical method (e.g., SP, induced polarization, etc) to directly detect the Chromium VI plume at the 100-D area is very unlikely to succeed and in my opinion is not worth pursuing. It is highly unlikely that even the most contaminated soil/water at the site will generate a detectable geophysical anomaly/signal. Although geophysical methods are unlikely to directly detect the Chromium sources integrated geophysical surveys can be used to more accurately and completely define the subsurface structure. This improved characterization of the subsurface should then be very useful for guiding and interpreting the drilling and cone penetrometer (if possible) measurements which can be used to identify the source areas.

As stated above, the proposed plan of using some yet-to-be-determined geophysical method (e.g., SP, induced polarization, etc) to directly detect the Chromium VI plume at the 100-D area is very unlikely to succeed and in my opinion is not worth pursuing. However, an alternative plan of using geophysical methods to better characterize the subsurface structure which would help to better define a conceptual model for the site would be an important contribution to the “systems approach” to the clean up of the 100 D Area site.

Implementation Strategy:
I would recommend the following approach for using geophysical methods to better characterizing the 100-D area site:

A. Synthesize all available information to develop a preliminary conceptual model for the site which will then be used to guide further exploration/characterization efforts
1. Summarize the historical use information for the site (complete?)
2. Define the subsurface infrastructure such as pipes, tanks, which may have been used to transport and store the contaminant (complete?). If it is feasible/practical to remove these structures then remove them.

3. Based upon the available well data and cores develop preliminary hydrogeological and geochemical conceptual models for the site.

B. Based upon the preliminary conceptual model a team consisting of a hydrogeologist, geochemist, and a geophysicist should develop an exploration plan for further characterizing the site. This plan should focus on using proven methods to better define the subsurface structure as opposed to more difficult and speculative efforts such as trying to directly detect the contaminant sources using geophysical methods. This exploration plan could be in the form of a new/revised proposal.

Based on my limited knowledge of the site I would propose the following items be included in the exploration plan:

1. If possible, log all available wells. I realize that nearly all of the wells at the site are steel cased wells which will exclude the electrical geophysical logs. However, it may be possible to use induced-neutron gamma ray spectrometry (e.g., Herron and Herron, 1996) to obtain high resolution geochemical logs of cased holes which can also be used to infer the formation lithology and even hydrogeological parameters
2. Perform reconnaissance surveys using EM methods (e.g., Geonics EM-31 and EM38).
3. If the location of metal pipes and tanks are unknown perform magnetic surveys to locate them.
4. Use GPR (it is relatively inexpensive) to map the near surface (top 30 feet) fill. This information in conjunction with the EM and magnetic data may help to guide the cone penetrometer pushes away from large boulders or objects that would impede the pushes.
5. Use high resolution seismic reflection (either between holes like is being done in the 200 West Area by Zseis or from the surface if possible) to map the lithology/structure between the logged wells.
6. As warranted, use electrical resistance tomography (ERT also called High Resolution Resistivity HRR in some of the previous reports by Hydrogeophysics, Inc.) and perhaps Induced Polarization to further characterize anomalous areas identified, for example, in the EM surveys.
7. Drill new holes to test/confirm the conceptual model and to provide access for further cross-well geophysical imaging. If possible, these new wells should be lined with PVC instead of metal to facilitate the geophysical imaging.
8. , and GPR to image between the logged wells. If PVC wells are available these methods can also be used to image between

Proposed Performance Metrics:
The performance metric of most relevance to the geophysical studies is how will/does the information gathered from the surveys help to improve the conceptual model for the site. And furthermore, how will/does this improved understanding help to better manage the remediation of the site.

Summary Evaluation:
The proposed plan of using geophysical methods to directly detect the Chromium VI plume at the 100-D area is very unlikely to succeed and in my opinion is not worth pursuing. However, an alternative plan of using geophysical methods to better characterize the subsurface structure which would help to better define a conceptual model for the site would be an important contribution to the “systems approach” to the clean up of the 100 D Area site. In my opinion, the proposed “systems approach” to the cleanup problem will be inadequate without such an effort to better define the subsurface structure at the site.

Reviewer #7

Target Plume/Area: Cr / 100 Areas

Proposal Title: Cr Source ID

Technical Basis of the Proposal:

General

-- This project is generally consistent with previous peer reviews and recommendations. It fits in to a systematic "blended" approach to the challenge of Cr near the Columbia River. The proposal provides a good descriptive justification of the need for source identification and I support that goal entirely.

The proposal provides little information on what tools may be used or what physical, chemical or electrical signal will be measured and why. This is a major weakness and may result in re-scoping. The proposal consists of $40K evaluation of potential geophysical technologies followed by doing it the traditional way if the evaluation does not identify any promising technologies. This is not an overtly bad strategy, it just may not be justifiable. One problem with this approach (e.g., past attempts to develop tritium water treatment based on hydrogen isotope separation) is that marginally promising ideas might be performed and utilize significant portions of the investment with minimal potential to identify the sources.

Past source identification efforts in the 100 Areas at Hanford included detailed process and historical evaluation, drilling, trenching and correlating potential sources with groundwater plumes. None of these has yielded a high enough concentration (Cr(VI)) zone to "source" a plume with concentrations as above 1000 ug/L in some areas. A major assumption and potential problem with this interpretation is that the past studies are based on a limited number of cores and high total Cr concentrations were found in several of the cores. The conclusions of these past studies were that the Cr source had not been found, <u>even in areas where the soil was visibly yellow and discolored</u>. The conceptual model, or conceptualization, of what an expected Cr source would look like is presently weak and does not support moving ahead with techniques like geophysics -- Hanford should examine and understand the existing data and develop a clear conceptualization as a prerequisite to moving forward on a source identification activity. Note that earlier studies showed a marked difference in Cr(VI) concentrations in the soil boring depending on the extraction method used (alkaline leach << distilled water and microwave) and there was minimal follow-up to examine the actual extraction efficiency of either method for Cr(VI). Also, there was minimal follow-up on why total chromium was enriched versus Cr(VI) in samples where the source was presumed to be a high strength acidic Cr(VI) solution. Moreover, the assumption that the excess Cr was converted to Cr(III) by interaction with ferrous minerals and organics in the soil was not examined further, nor was the potential for Cr(VI) to occur at ppb levels in the presence of high levels of Cr(III). See additional geochemistry comments below.

Alternatives to the geophysics include: 1) do more of the old fashioned way -- drilling or trenching, more historical and process evaluation, and more plume correlation. One approach that I have seen much success with is adding in plume depth to the correlation and noting that the source is near the area where the plume is at the water table – unfortunately, this requires a relatively stable water table, modest heterogeneity and a large plume – none of these factors are present at this site. 2) Mesoscale interrogation of the field site using cross well injection extraction tests or push pull tests (if a solution can be devised that would provide a signal), 3) soil gas surveys (if a gas signal can be correlated to the presence of the waste (acid-CO_2?, carbon isotopes, hydrogen isotopes?), 4) soil gas or borehole logs to determine if there is a signal due to changes in uranium distribution under the influence of acidic chromate solution, etc.

Heterogeneity and culture, particularly a thick zone of heterogeneous rubble, will limit any surface geophysics technique. Borehole geophysics will probably require significant drilling (in which case one might just plan to sample). Need to install PVC or fiberglass casing.

High total chromium zones (e.g., >500,000 ug/Kg) were identified in earlier studies (but mostly in the assumed form of Cr(III). There are several possible explanations, including but not limited to: 1) The total chromium values are actually Cr(VI) but the extraction efficiency of the alkaline or microwave distilled water leach is poor for the particular chemistry and mineralogy of the Cr in the sample (e.g., associated with carbonates, etc.); or 2) the total Cr(III), potentially the thermodynamically dominant form in this redox setting, could release sub ppm Cr(VI) based on thermodynamic and kinetic equilibria…. Cr(VI) in the discolored and elevated total Cr soil samples was measured at 50-150 ug/L. Could the Nernst equation be combined with aqueous solubilities and speciation to determine the expected release of Cr(VI) from a Cr(III) zone? These are important conceptual issues. Is the source zone dominantly Cr(III)? If it is a Cr(III) zone contributing a low but steady Cr(VI) leach to the groundwater, then potential treatment or stabilization options might include a simple shift of redox conditions, or addition of a long lived electron donor. Alternatively, if the source zone Cr is in the form of Cr(VI) that is not being efficiently extracted by alkaline or distilled water leaching, then alternative concepts for stabilizing and detoxifying the source would result.

Cost appears reasonable but the expert panel may not be needed and could be changed to a more integrated approach.

Implementation Strategy:
Schedule is generally reasonable. Proposed technology panel is unlikely to identify a silver bullet in geophysics or even a good weight of evidence geophysics suite.

Proposed Performance Metrics:
Little detail here – it is deferred to the geophysics technology panel within the project.

Summary Evaluation:
Good part of the strategy. Consider alternative of traditional or exploration geochemistry approaches.

Reviewer #8

Target Plume/Area: Chromium Source at the 100-D Area

Proposal Title: Refine Location of the Chromium Source at the 100-D Area

Technical Basis of the Proposal:
Direct detection of the chromium plume is not a reasonable expectation for geophysical methodologies. An attainable goal is the definition of the geological/hydrological setting than can be used as a framework for the locating the chromium source

Implementation Strategy:
Geophysical methods are cost effective tool that should be used in an integrated program of geochemical, hydrological and geophysical investigation

A proposed sequence would included:

1) Reconnaissance geophysics (quick & dirty) survey such ground conductivity meter (GCM), magnetics, and GPR. The GCM and mag would be useful to define surface clutter that may make deeper surveys problematic.
2) Low-frequency GPR would be useful to aid in the locating drill holes for borehole and/or cone penetrometry.
3) Neutron or other appropriate logging of existing holes.
4) A full 3D resistivity survey would be useful in defining heterogeneity of the geology and related hydrology
5) Subsurface resistivity measurements can be obtained with penetrometry push technology
6) Cross-hole geophysics (ERT, GPR, seismic) can be performed in optimally placed boreholes for high resolution imaging
7) Geophysical anomalies correlated with geochemistry and borehole geology for calibration.

Proposed Performance Metrics:
The baseline has been to drill holes and has not been successful in establishing a framework of finding a source term. Implementation of a geophysical program would not guarantee the location of the source, but would provide a context to guide further drilling

Summary Evaluation:
The proposal as stated is a no-go. However with some refining, as noted above, geophysics has a significant role to play in establishing the baseline for which other investigations and decision can be made.

APPENDIX D

Chromium Vadose Zone Characterization and Geochemistry

Target Plume/Area: Chromium/Hanford 100D Area

Proposal Title: Chromium Vadose Zone Characterization and Geochemistry

Reviewers: Brian Looney (lead), Todd Anderson, Dawn Kaback, and Gene Leboeuf

Summary Evaluation

The proposal addresses a valid technical need to supplement and support a systematic approach to addressing Cr(VI) at the 100D Area of Hanford. The review panel felt that this proposal, in combination with the supporting Fluor field campaign, is a significant improvement compared to the earlier proposed source identification strategy that relied primarily on geophysics. DOE should consider funding this effort – we recommend that the proposers consider the technical comments and recommendations as they finalize the work plan and schedule.

We recommend that this work should be better integrated with related site activities, particularly the Fluor field sampling study as well as ongoing removal actions such as the removal of chromate transfer lines. Such integration may require modifying schedules, sharing samples, or developing interim products to share with others working at the site. A principal objective of this geochemical effort should be to provide key information to refine the conceptual model related to chromium transport and accumulation in vadose zone and shallow groundwater impacted by high strength chromium sources.

The project is likely to provide a better understanding of Cr(VI) sources in vadose zone sediments, particularly if solid phases exist. This would be of interest from a geochemical standpoint and a practical standpoint. Clear scientific hypotheses should be postulated for each task and the tasks should be reviewed for the potential value to conceptual model development. The improved conceptual model needs to be built using a phased approach, so that information obtained early on can be utilized to support the Fluor Hanford field investigation of the location of chromium sources in the 100-D Area.

Right now, a large number of physical and chemical characterization techniques and column studies are proposed. The techniques selected are generally reasonable and were supported in the peer review. As noted above, the proposal is currently organized into a loosely coordinated series of laboratory experiments-- more description of why these techniques are being done and how the results will lead to an improved conceptual model.

To integrate with other activities, the tasks should begin by trying to understand the forms and phases of the Cr in the vadose zone and then later address its leachability. But the tasks in the proposal appear to be in the opposite order with a heavy focus on leachability with the column studies. Various alternative recommendations are included in the individual reviewer comments.

The reviewers expressed some skepticism that chromium could be loaded into the columns in a manner that was representative of field conditions and recommended that the researchers focus on real contaminated sediments where possible.
The proposed approach is an appropriate part of a “defense in depth” concept for immobilizing chromium in the subsurface before it reaches the Columbia River. The proposed study area is upgradient of the proposed biological reduction effort and the “to be repaired” ISRM barrier. Identifying the source location would be a substantive step toward source removal or engineered immobilization.

Technical Basis of the Proposal:
The proposal is based upon valid and appropriate science. The goal of the project is to characterize chromium source areas in the vadose zone, including understanding the mechanisms for its accumulation and leachability over time. The technical likelihood of the stated-desired outcome is good, if there is a concerted effort to utilize the data from the individual experiments to build the conceptual model. Currently the proposal reads more like a series of laboratory experiments, than a proposal to build a conceptual model. *Some discussion of how these individual experiments will be used to build the conceptual model needs to be included*. (Reviewers 2 & 4)

The project fits well with the overall proposed activities for investigation and treatment of chromium in the 100-D Area at Hanford (All Reviewers)

The proposed approach is reasonable, although focus is heavy on understanding mechanisms, with limited attention on geochemical characterization that might support delineating sources in the field through methods other than drilling, such as geophysics, tracer tests, etc. Please note the comments from the March 2006 review for specifics. (Reviewer 1, 2 & 4))

Strong integration with the various sampling activities is needed to assure that the materials will be available for study – this is implied in the proposal but needs to be confirmed and documented. (Reviewers , 3 & 4).

The column studies (Task 3) are generally well conceived and are potentially important to the overall objectives. Nonetheless, the reviewers had many comments on this portion of the work. These included recommendations to emphasize contaminated sediment collected from the field rather than trying to recreate them with saturated columns over a short period of time (Reviewers 2 & 4), recommendations to emphasize the macroscale and microscale studies to provide an early conceptual model deliverable back to Fluor to support the field effort (Reviewer 2), recommendation to consider more emphasis on small batch leaching tests rather than the column studies (Reviewer 4), cautions about the potential for confounding geochemistry in the columns (Reviewer 4), concern that the temperature studies would be of limited value (Reviewers 2 & 4), etc.

There were several positive comments and some concerns/recommendations related to the geochemistry and modeling (All reviewers). Example concerns include: potential lack of availability for thermodynamic data on barium chromate minerals (Reviewer 2), recommendations for analytes and methods (Reviewer 2), additional literature references (Reviewer 4), etc.

Implementation Strategy:
There were several comments related to schedule and sequencing – Several reviewers suggested that macroscopic characterization should be completed first and reported to support and interim conceptual model development. The longer-term equilibration studies and column studies don't necessarily need to be completed before the conceptual model can be constructed. A phased approach should be used so information can be relayed to Fluor Hanford early on, so they can pursue the drilling program, before this project is completed. (Reviewers 2 & 4)

The budget appears reasonable.

Proposed Performance Metrics:
This effort will greatly facilitate the ability to fill existing knowledge gaps. Limited performance metrics are currently included in the proposal (e.g., Tasks 3, 4 & 5).

Better integration, clear hypotheses and a plan for conceptual model development from the disparate data, and interim deliverables need to be developed.

Reviewer #1

Target Plume/Area: Chromium/Hanford 100 Areas

Proposal Title: Chromium Vadose Zone Characterization and Geochemistry

Technical Basis of the Proposal:
Is the project or activity based on appropriate and valid science?
Yes. The project is based on sound science and takes an approach that is quite similar to investigations of uranium fate and transport in other areas of the Hanford site. In the Hanford subsurface, Cr(VI) is not expected to adsorb to subsurface materials and there is limited availability of reductant (Fe(II)) to reduce Cr(VI) to an immobile form. Therefore long term sources of Cr(VI) contamination are likely to be found in the vadose zone, either as "trapped" soluble species in saturated pores in an otherwise unsaturated vadose zone or precipitated as soluble or semi-soluble phases in fully unsaturated areas. There is a need to understand just how Cr(VI) is retained in the vadose zone in order to forecast future transport behavior in the subsurface.

What is the technical likelihood of the stated-desired outcome? The project is likely to provide a better understanding of Cr(VI) sources in vadose zone sediments, particularly if solid phases exist. This would be of interest from a geochemical standpoint. Will the proposed speciation techniques (APS studies) identify unknown Cr species? Will the beam at the APS produce reduced Cr species and how will this be controlled for? Are there similar studies planned for documenting the extent of reduced Cr species? Addition of reductant is the planned treatment technique in these areas is it not?
There is little information on how the results of the investigation will be used other than to develop a conceptual model. Are these results to be incorporated into a site wide model of Cr(VI) transport to the River?

How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable? The project meshes well with the proposed drilling activities to determine the Cr(VI) sources in the 100-D areas and other areas at this site. Samples from the drilling activities in the 100-D Area will provide ready sources of material for use by this project. Also, this project brings added value to the Cr(VI) Source Location efforts by providing additional information on the speciation and potential phases of Cr(VI) that may exist under conditions found in the vadose zone.

What about evaluating, at least from a lab perspective, possible Cr(VI) immobilization techniques for these source zones and/or identifying reduced Cr species?

What are the risks or key uncertainties in the proposed action(s)?
Identification of novel Cr species/phases will undoubtedly require more investigation.
Time at the APS will need to planned for well in advance. The APS work is a key element of this project because this technique can identify solid phases of Cr(VI) that may be present in these sediments. Identification of novel solid species could require more time to interpret the results.

The approaches to evaluating sources of Cr(VI) in the vadose zone are appropriate. The Leads have experience running these types of experiments before. I think that reasonable results will be obtained from proposed work but I am not sure how the results will be used and who will use them. I assume the report will lay out a conceptual model for Cr(VI) in vadose zone source sediments. Who is waiting to receive such as report, the cleanup contractors?

Are there clear examples of alternative ideas or proposals that should be considered? The approach taken to characterizing and identifying the sources of Cr(VI) in vadose zone sediments is appropriate. These studies could get much more complicated and much more intricate and detailed but the level of sophistication presented here is appropriate to the tasks at hand.

Implementation Strategy:
(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work?
This project will obtain subsurface samples from the 100 Area (sites A, B and C) and from the 100-D Cr source identification project and will require good timing and coordination with that project. It is unclear how many 100-D samples will be processed using this approach.

Proposed Performance Metrics:
(Does the proposed project or activity represent a significant improvement compared to the baseline? Does the project improve the protection of the Columbia River now or in the future? Are there measurable parameters that would document performance? Are these included in the proposal?) Yes. The project will produce data that will be used to develop a conceptual model of the sources of Cr(VI) in the vadose zone at the 100 Area. It is important to understand the geochemical nature of source zone Cr(VI) in order to make reasonable forecasts of the potential for Cr(VI) mobility and/or to design Cr immobilization strategies.

Summary Evaluation:
This appears to be an additional project that compliments the drilling activities to be undertaken to find the source zones of Cr contamination in the Hanford 100 Area. The goal of the project is to analyze subsurface samples collected during drilling to more fully evaluate the fate of Cr in vadose zone source sediments at this site. Cr(VI) is thought to be sequestered in these sediments either as soluble salts in unsaturated pores or trapped as a soluble species within saturated pores in otherwise unsaturated vadose zone strata. This project seeks to investigate these two possibilities and develop a conceptual model of Cr(VI) in source zone sediments, similar to what has been done for uranium at other Hanford Areas, to aid descriptions of the fate and transport characteristics of Cr(VI) at this site. I find the laboratory analyses to be appropriate to the task(s) of developing a conceptual model of source zone Cr(VI) contamination using the grab samples from the proposed sites indicated in the proposal (sites A, B, C). However the extent to which other samples made available to the project from the drilling activities in the 100-D area will be analyzed is unclear. How many of these 100-D samples can be screened given the current budget for this project? Also, if the Cr(VI) contamination in this area is all of the same chemical

"character" (i.e. acidic solutions discharged to the subsurface) then the column studies should be widely applicable across the site. If there are known instances where the chemical nature of Cr(VI) that was introduced into the subsurface is different, this obviously may require additional investigation.

Overall, I find this project to be an appropriate approach to developing information about the Cr(VI) source zones in the 100 Area. The column leaching studies should be particularly interesting. I recommend that this project proceed.

Reviewer #2

Target Plume/Area: 100-D Area Chromium Plume

Proposal Title: Chromium Vadose Zone Characterization and Geochemistry

Technical Basis of the Proposal:
The proposal is based upon valid and appropriate science. The goal of the project is to characterize chromium source areas in the vadose zone, including understanding the mechanisms for its accumulation and leachability over time. The technical likelihood of the stated-desired outcome is good, if there is a concerted effort to utilize the data from the individual experiments to build the conceptual model. Currently the proposal reads more like a series of laboratory experiments, than a proposal to build a conceptual model. *Some discussion of how these individual experiments will be used to build the conceptual model needs to be included.*

The project fits well with the overall proposed activities for investigation and treatment of chromium in the 100-D Area at Hanford. The proposed approach is reasonable, although focus is heavy on understanding mechanisms, with limited attention on pursuing methods for delineating sources in the field through methods other than drilling, such as geophysics, tracer tests, etc. and limited attention on building the conceptual model. Please note the comments from the March 2006 review for specifics.

The key uncertainty related to this proposal is in obtaining the appropriate samples in the 100 B/C Area and also in the 100-D Area. There is a statement in the proposal related to the 100 B/C Area that "excavation of both sites is possible and may be performed in a cooperative venture." This seems a little loose and needs to be confirmed, because without these samples, the project cannot be completed. This proposal describes the approach recommended by the March 2006 peer review panel. As such, no alternatives were considered

The tasks should begin by trying to understand the form of the Cr in the vadose zone and then later address its leachability. But the tasks in the proposal appear to be in the opposite order with a heavy focus on leachability with the column studies. Understanding of the form of the Cr could impact the design of the column studies.

I don't really understand the goal of Task 3 and how fits with field conditions. It appears to investigate Cr transport under saturated conditions. How does this answer the question about transport and accumulation in the vadose zone? This task appears to take vadose zone samples containing high concentrations of Cr and submit them to leachability tests assuming saturated conditions. I don't understand why saturated conditions are assumed for this testing. Costs could be reduced by leaching only contaminated sediments, rather than trying to recreate original conditions. What is the chemistry of the influent solution for the contaminated sediments? Because I am having difficulty with understanding whether you are trying to simulate unsaturated or saturated conditions, I don't know whether the leachate should simulate vadose zone pore water or groundwater. If groundwater is to be simulated, it should be contaminated groundwater that contains nitrate, etc., as would be present in the 100-D Area?

I also don't recommend the tests at different temperatures? I don't see the application for the two elevated temperatures in the field. This could also reduce costs.

Macroscopic characterization of pore water in existing samples should be first completed and reported to allow initial construct of the conceptual model. The longer-term equilibration studies don't need to be completed before the conceptual model can be constructed. A phased approach should be used so information can be relayed to Fluor Hanford early on, so they can pursue the drilling program, before this project is completed. The field moisture capacity water contents are most important and the other two could be cut from the program to reduce funding needs. What is the purpose and field application for all three water contents?

Are there sufficient thermodynamic data for chromium minerals, such as the $BaCrO_4$ and the $BaCrO_4$-$BaSO_4$, in MINTEQA2 to perform the geochemical modeling? If not, the geochemical modeling may not provide useful information and could be deleted from the task. Even if thermodynamic data for these phases exist, a decision on the modeling should be reserved until after results are obtained from the micro-scale characterization. I recommend performing the micro-scale characterization as soon as possible after the initial characterization. That is, it should be task 3 and task 3 should be task 5.

Contaminated soil sample analyses should include total iron (can this be done with XRF of solid materials?) and mineralogy (XRD) (I see this is in Task 5).

Implementation Strategy:
Sequence and timing of activities is currently **not** appropriate, as Task 5 should be conducted before Tasks 3 and 4, and Task 3 should be conducted last. In addition, the length of time shown for Tasks 4 and 5 is excessive. These activities should be concentrated into shorter time periods, with perhaps a period early for the 100 B/C Area and a later time for samples from the 100-D Area.

The budget and level of effort is **slightly elevated.** Some small cuts in the proposed activities, as described in the text above, could result in a reduction in the budget. In addition, what is the purpose of the ~$4,000 in travel, ~$24,000 in ODC, and ~$17,000 in direct materials?

Proposed Performance Metrics:
There is little information in the proposal about performance metrics. These should be developed on a task by task basis, with clearly stated objectives and performance metrics. In this way, we can ensure that each of the tasks is answering an important question relevant to understanding chromium migration and accumulation in the field.

Summary Evaluation:
In summary, the proposal addresses a valid technical need to supplement the Insitu Redox Manipulation Barrier through investigation of potential chromium sources up-gradient of the barrier, to enhance understanding about chromium migration and accumulation mechanisms. I recommend that the work be conducted, after each of the tasks is reviewed for potential impact to the conceptual model. The conceptual model needs to be built using a phased approach, so that information obtained early on can be utilized to support the Fluor Hanford field investigation of the location of chromium sources in the 100-D Area. More emphasis should be placed on how the data from each of the tasks will be input to the conceptual model. There is not enough emphasis on building the conceptual model in the proposal, but instead it reads like a series of laboratory experiments. Some reduction in budget may be possible, if some of the activities, such as elevated-temperature experiments, can be cut from the scope.

Reviewer #3

Target Plume/Area: 100 B/C/D Areas

Proposal Title: Chromium Vadose Zone Characterization and Geochemistry

Technical Basis of the Proposal:
Is the project or activity based on appropriate and valid science?
Yes. Proposed work involves the use of various state-of-the-art analytical techniques to facilitate chromium leaching and retention characteristics representative of Hanford Site conditions. Efforts are focused on using contaminated sediments from three separate 100-Area locations to improve understanding of leaching characteristics of Cr(VI), including column leaching tests with both contaminated and uncontaminated Hanford sediments, plus microscopic and macroscopic characterization studies, to assist in construction of a conceptual model of (Cr(VI) geochemistry at Hanford. This enhanced conceptual model will further facilitate current efforts to accelerate cleanup of Cr (VI) contamination near the Columbia River through a variety of "defense in depth" measures.

What is the technical likelihood of the stated-desired outcome? Very good. Proposed work focuses on collection of contaminated sediments via excavation (100 B/C Areas) and drilling (100 D Area; it also serves as a companion effort with the Pacific Northwest Laboratory proposal "Refine Location of the Chromium Source at the 100D Area and Support a Geochemical/Mineralogical Study of Chromium in the Vadose Zone"). Proposed employed methods are reasonable, with the proposed team possessing the requisite skills and experience to conduct such activities.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? This effort represents an integral component of an overall systems-based approach to remediate the chromium plume in the 100 Area. Specifically, this effort is geared towards developing a conceptual model for Cr(VI) in the 100 Area. Additional projects include (i) reinforcing an existing insitu redox manipulation (ISRM) barrier placed in the 100D area in 1999; (ii) immobilization of chromium in the ISRM plume by circulating a strong reductant in the aquifer; (iii) enhancing the current pump and treat effort by replacing the ion exchange treatment method with electrocoagulation; (iv) remediation of waste sites along the Columbia by 2012 through the River Corridor; and (v) drilling small-diameter wells to further characterize vadose zone soils and nearby groundwater. This suite of proposed activities is oriented towards generating a reduction environment. This proposal will further facilitate our understanding of mechanisms controlling Cr(VI) fate and transport in the Hanford 100-Areas.

Is the proposed approach reasonable and practicable?
Yes. There is a clear need to better understand the underlying mechanisms most responsible for observed Cr (VI) leaching/retention at Hanford. The proposed approach seeks to use both contaminated and uncontaminated sediments to better elucidate expected behaviors based on site geochemistry, lithology, and time of exposure (aging process).

What are the risks or key uncertainties in the proposed action(s)?
Primary risk lies with the ability to effectively collect samples from the 100-D Area, especially if small-diameter drilling is not funded. Uncertainties primarily tie with the ability of selected uncontaminated sediments proposed for use in column leaching studies to properly represent the spectrum of materials present in 100-Areas.

Are there clear examples of alternative ideas or proposals that should be considered?
The proposed advanced characterization tasks identified in the proposal are reasonable, with no clear alternative methodology to obtain similar information.

Implementation Strategy:
Is the sequence and timing of activities appropriate?
Yes.

Can the technology be implemented cost-effectively?
Yes.

Is the budget and level of effort appropriate for the proposed work?
Yes. The budget of $500k appears reasonable for an 18 month study of this depth. Budget should be revised should drilling in 100-D Area is not approved.

Proposed Performance Metrics:
Does the proposed project or activity represent a significant improvement compared to the baseline?
Yes. The current baseline lacks detailed geochemical models to predict chromium fate and transport under conditions present at Hanford's 100-Area. This effort will greatly facilitate the ability to fill existing knowledge gaps.

Does the project improve the protection of the Columbia River now or in the future?
Yes, success of this effort can assistance in reducing the time, expense, and potential for migration of the chromium plume to the Columbia River in the future.

Are there measurable parameters that would document performance? Yes. Tasks 3, 4, and 5 each represent specific activities aimed to quantify

Are these included in the proposal?
Yes.

Summary Evaluation:
This proposal represents an important effort to further define geochemical influences on Cr(VI) leaching/retention in representative Hanford 100-Area materials. Strong support for this activity

from this reviewer, even if the proposal for small-diameter drilling in the 100-D Area is not funded.

Reviewer #4

Target Plume/Area: 100-D Area Chromium Plume

Proposal Title: Chromium Vadose Zone Characterization and Geochemistry

Technical Basis of the Proposal:
The proposal is based upon valid and appropriate science. The goal of the project is to provide key geochemical information about Cr(VI) in sunder the site-specific conditions of the Hanford and Ringold Formations near the Columbia River (disposal history, geology, hydrology, removal actions etc.).

This work is supposed to inform and help provide the conceptual basis for the related drilling activities that focus more specifically on 100D source identification. A better description of how these projects will be related would be useful in finalizing the work scope. In particular, the goals of the evaluation should be formatted into hypotheses that will directly support development of an improved conceptual model of total chromium as well as Cr(VI) – this conceptual model would then better inform the field activities. Right now, a large number of physical and chemical characterization techniques and column studies are proposed. While the techniques selected appear generally reasonable, there is little description of why these techniques are being done and how the results will lead to an improved conceptual model. Obtaining and tabulating lots of geochemical data on Cr in these sediments is not useful unless the next step is made.

It was encouraging that samples that are sufficiently high in total chromium (and high in Cr(VI) to be the source to groundwater containing ppm levels of Cr(VI) have been identified and are being investigated. Perhaps the current field activities excavating chromate transfer lines will shed additional light on past sources.

I would encourage the investigators to carefully select, test and implement their methods to make sure that the measurements of Cr(VI) versus other oxidation states are accurate under the range of expected site specific conditions (e.g., impacts of carbonates, etc.).

Tests related to the imprint of acid alteration (mineral leaching or diagenesis) on the sediments are an important component of the effort. This portion of the work might suggest field screening ideas or potential geophysical signals.

The geochemical references were appropriate and useful. Another reference that might be interesting to look over is Kozuh et al., 2000. Reduction and oxidation processes of Chromium in soils, ES&T, 34:1, pp 112-119 (this article discusses conditions and rates of Cr(VI) reduction by organic matter, Fe(II) and other electron donors as well as Cr(III) oxidation by Mn oxides in a variety of soils).

The column studies (Task 3) were generally well conceived from a basic science and theory perspective and they appear to be relatively cost effective if the equipment is already in place. I am not fully convinced that they are the best way to achieve the objectives for this conceptual model development and source identification for 100D area. Specifically, I am skeptical that sediments loaded with Cr done in a continuous flow-through mode will resemble the field conditions where the contaminants were likely loaded in an episodic or slow fashion over many years and then subjected to post depositional driving forces like rainfall. I think that using real field sediments and doing the leaching on small samples in a batch mode or semi-batch mode (measuring release versus time from the real samples) might be more representative and potentially less expensive. Also, while I really like the traditional engineering approach to the column studies (e.g., stop flow events to help determine mass transfer controls and temperature control to help determine mechanisms), I am skeptical that mechanisms such as diffusion processes on the scale of the planned columns & flowrates will be able to be distinguished from each other due to potential variability and uncertainty (and due to the fact that there is potential for confounding changes in reduction and/or oxidation processes that might be influenced by temperature). I recommend that the proposers consider alternatives to the planned column studies using real contaminated sediments and that some of the other tasks be emphasized in the early stages of the effort.

Implementation Strategy:
Generally reasonable, consider resequencing to emphasize geochemical evaluation of real contaminated samples and to de-emphasize column (or alternative) leaching studies.

The budget and level of effort is generally reasonable, some reduction may be possible based on technical recommendations.

Proposed Performance Metrics:
Performance metrics are MIA and should be developed as the work plan is finalized with DOE – in particular, the integration of this work with the planned field work and the manner in which the conceptual model is refined needs to be laid out in a measurable fashion.

Summary Evaluation:
The proposal addresses a valid technical need and it is generally consistent with the earlier chromium source identification recommendations of the independent peer review panel. More emphasis on building the conceptual model and linkage to the planned field campaign are needed.

APPENDIX E

Refine Location of the Chromium Source at the 100-D Area and Support a Geochemical/Mineralogical Study of Chromium in the Vadose Zone

Target Plume/Area: Chromium/Hanford 100D Area

Proposal Title: Refine Location of the Chromium Source at the 100-D Area and Support a Geochemical/Mineralogical Study of Chromium in the Vadose Zone

Proposal Reviewers: Brian Looney (lead), Todd Anderson, Dawn Kaback, and Gene LeBoeuf

Summary Evaluation:
The proposal addresses a valid technical need for source location delineation as an important part of a systematic approach to addressing Cr(VI) at the 100D Area of Hanford. The review panel felt that this proposal, in combination with the supporting geochemistry study, is a significant improvement compared to the earlier proposed source identification strategy that relied primarily on geophysics. DOE should consider funding this effort – we recommend that the proposers consider the technical comments and recommendations as they finalize the work plan and schedule.

The work plan should be better integrated with related site activities, particularly the geochemistry study and ongoing removal actions such as the chromate transfer lines. The conceptual model developments and data from the geochemistry study would inform and improve the field effort and coupling to ongoing removal actions might provide samples and access that would benefit the objectives while reducing costs. Such integration may require modifying schedules, sharing samples, or developing interim products to share with others working at the site.

The strategy and balancing criteria for selecting the borehole locations needs to be developed and documented (up front).

A more complete description of the analytes to be measured, the justification for those analytes, and the methods to be used is needed (up front).

More employment and use of historical geologic, soil sample, and groundwater monitoring information, including estimates of backward location and travel time probability distributions for the observed contamination is needed.

Performance metrics (e.g., What criteria will be employed to guide the location of the 7 wells?; What will define failure or success for well drilling, sampling, and monitoring?) are needed.

The proposed approach is an appropriate part of a "defense in depth" concept protecting the Columbia River from chromium contaminant. The proposed study area is upgradient of the proposed biological reduction zone and the "to be repaired" ISRM barrier. Identifying the source location would be a substantive step toward source removal or engineered immobilization.

Technical Basis of the Proposal:
The proposal is based upon valid and appropriate science.

The general strategy of moving upgradient (in the groundwater) to bracket the potential location of the source in the vadose zone or shallow groundwater is sound but is subject to significant technical uncertainty. The borehole locations selection criteria need to be developed and documented – see specific suggestions by all reviewers. This is particularly important because the costs for these shallow boreholes at Hanford are relatively high. The need for more rounds of drilling would significantly drive up total costs and if poor locations are selected these costs would not be justified (Reviewer 1).

The proposed work would benefit from better integration with the conceptual model development in the related geochemistry proposal, as well as with ongoing activities (such as the excavation and removal of the chromate transfer lines). Work may need to be scheduled to correspond to interim conceptual model deliverables of parallel field activities (reviewers 2 & 4) An example of this integration might be ext sampling during any ongoing removal actions (e.g., of chromate transfer lines) – this might provide direct access to highly contaminated sediments and the ability to opportunistically extend samples down several meters using hand coring techniques in environments where obstructions are not encountered. Because the source remediation contractor is likely limited in their scope to gross analysis of chromium, the supplemental funding would provide a real opportunity for measuring additional parameters that would provide key data for refining the source location (Reviewer 4).

The proposal lacks detail on how existing information will be effectively employed to further refine location of the source plume (all reviewers). The proposal did not address specific objectives on modeling efforts. For example, statements such as "modeling will use the groundwater chromium data, coupled with analysis of groundwater flow in the area, to refine a conceptual model for chromium in the vadose zone and groundwater" insufficiently describe modeling objectives, methodologies, and performance measures. Use of existing plume and geology information coupled with forensic modeling might be a more promising approach (Reviewer 3).

A more complete listing of analytes is needed as well as the logic and justification. (Reviewers 2 & 4). Parameters should be included to allow estimation of bulk responses to potential geophysical tools to determine if any signal might be able to be used for delineating chromium (or perhaps past exposure to strongly acidic solutions). (Reviewers 1, 2, & 4). If the data showed potential utility for geophysics in the future, then "hit and miss" drilling can be minimized (Reviewer 1). The March 2006 review panel recommended consideration of other analytes and possible tracer tests that could only be planned based on the 100 B/C Area work.

The selection of the drilling technology generally appears reasonable and is justified in this shallow but challenging setting. The plans should allow for refusal and have a strategy for rapidly and cost-effectively moving to alternate locations for additional penetration attempts (All Reviewers). One reviewer recommended consideration of excavation to the base of the debris and then use of direct-push drilling techniques (Reviewer 3). There is no mention of standard techniques such as GPR/CMT to assist in well location. (Reviewer 3).

Weekly groundwater sampling may not be necessary – weekly sampling should be discontinued after concentrations recover from the installation "trauma" and stabilize and then a longer timeframe employed (e.g., monthly or even quarterly). (Reviewers 2 & 4). This project has minimal need for hourly groundwater level data and automated logging/access and the proposal should not describe such a system as an integral part of refining the chromium source location (Reviewer 4).

Implementation Strategy:
The sequence and timing of activities should be integrated with the geochemistry study and other activities underway in the 100 D Area. All plans, drilling locations, sampling strategies, analytes, etc. should be developed based on a conceptual model for movement and accumulation of chromium in the vadose zone and shallow groundwater. This may require developing interim deliverables so that information and samples can pass between efforts. (All Reviewers)

Additional "preliminary" effort should be made to make use of existing plume and geology information coupled with forensic modeling. (Reviewer 3)

The budget is high at $650,000 for only seven wells. Also $95,000 for planning appears to be high. (Reviewers 1 & 3)

Proposed Performance Metrics:
There is no information in the proposal about performance metrics. It appears that location of the head of the chromium groundwater plume and the source in the vadose zone are goals, but no groundwater or soil chromium concentrations were identified as being definitive of these goals. There is no description of what the head of the plume would look like in map view or what a vadose zone source area would look like in terms of soil concentrations. This further illustrates the need for the conceptual model based upon data from a known source area. This conceptual model is needed so that when boreholes are drilled and samples collected, appropriate analytical measurements will be made. (Reviewer 2)

Over the long-term, identification and treatment of the source areas of Cr contamination is the most important step to protecting the Columbia River from further Cr inputs. There are no guarantees that all of the source areas will be found but a search must be undertaken to find as many as possible. (Reviewer 1)

Reviewer # 1

Target Plume/Area: Chromium/Hanford 100D Area

Proposal Title: Refine Location of the Chromium Source at the 100-D Area and Support a Geochemical/Mineralogical Study of the Chromium in the Vadose Zone

Technical Basis of the Proposal:

Is the project or activity based on appropriate and valid science?
Yes. This is a revised proposal based on reviews from a panel of experts indicating that the use of geophysics techniques to locate the source of Cr in the vadose zone is not likely to produce definitive results. The subsurface in the 100-D Area particularly near the proposed test area (183-DR Head House) is complicated by a mix of D&D debris and buried foundations. All of these structures will likely complicate geophysical surveys leading to less than conclusive results. The revised proposal will utilize innovative drilling techniques to recover samples from the subsurface for laboratory testing to determine the presence or absence of Cr in vadose and saturated zone samples.

What is the technical likelihood of the stated-desired outcome?
Drilling and analyzing subsurface samples is the fall back technology if geophysics techniques are not likely to yield conclusive results. A panel of experts indicated that due to the complicated subsurface structures in the area, geophysical techniques are not likely to conclusively identify Cr source areas at this site. Therefore drilling operations will be performed to find the source areas. This is a "hit or miss" strategy that has a high probability of finding non-source areas but the results are demonstrably conclusive. Samples recovered from the subsurface either have Cr in them or not based upon the laboratory analyses. There is a reasonable chance based on some historical records and informed guesswork that some source areas will be identified by drilling in this area.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? The projected plan is part of an overall plan to remediate Cr contamination in the 100-D area by intercepting Cr in the subsurface before it gets to the river, immobilizing Cr in the upgradient groundwater plumes and stabilizing Cr in the source areas. This plan deals with finding and immobilizing Cr in the source areas and is integral to the overall plan.

Is the proposed approach reasonable and practicable? The approach is expensive, time consuming and "hit or miss" in terms of finding the source areas. It is, however, the only option available to conclusively demonstrate whether Cr contamination exists in the surface at this site.

What are the risks or key uncertainties in the proposed action(s)? A major risk is that the drilling techniques will prove to be ineffective in obtaining samples from the subsurface and a more robust (and more expensive) drilling technique will be needed. Also of concern is the very real chance that the drilling results will not identify the source areas and thus more drilling (and more funds) will be required.

Are there clear examples of alternative ideas or proposals that should be considered? No. Geophysics was offered as a method(s) to more cost effectively identify source areas prior to drilling but a panel experts did not think these techniques would yield conclusive results.

Implementation Strategy:
The timing and sequence is appropriate in light of the overall plan for the site. The budget is high at $650,000 for only seven wells. From tax payer's perspective this is offensive.

Proposed Performance Metrics:
If geophysical techniques (the original proposal) are considered the baseline then the proposed drilling is an improvement over the existing baseline, albeit an expensive improvement, in that the results obtained will be conclusive. Over the long-term, identification and treatment of the source areas of Cr contamination is the most important step to protecting the Columbia River from further Cr inputs. There are no guarantees that all of the source areas will be found but a search must be undertaken to find as many as possible.

Summary Evaluation:
In light of the panel review which indicated that geophysics measurements were not likely to conclusively demonstrate a location for the Cr source areas, the only conclusive option left was drilling/sampling/lab analysis. The workplan for drilling near the Head House in the 100-D area seems appropriate. The drilling techniques will be most useful in areas not likely to contain much D&D debris and/or foundations. Certainly push techniques alone will fail in the D&D/foundation areas. Perhaps the proposed new(er) techniques will fare better. What is the backup technique if the proposed drilling techniques do not work as planned? There was mention of these bore holes being prepared as monitoring wells for later incorporation into a groundwater sampling program. This is important particularly if source areas are found and treated to be able to demonstrate a treatment effect (i.e decreasing Cr concentrations after treatment of the source area). What additional cost will be incurred to obtain a variance to install these small diameter wells?
I recommend that this project proceed.

Reviewer # 2

Target Plume/Area: 100-D Area Chromium Plume

Proposal Title: Refine Location of the Chromium Source at the 100-D Area and Support a Geochemical/Mineralogical Study of Chromium in the Vadose Zone

Technical Basis of the Proposal:
The proposal is based upon valid and appropriate science. However, there is significant uncertainty associated with trying to find a vadose-zone source area and the head of a groundwater plume by drilling seven (or is it ten?) boreholes.

There are two significant technical issues associated with this proposal. However, they can be easily corrected. The first deals with lack of information related to the strategy for selecting borehole locations and the second deals with timing of the investigation, both further described below.

The proposal states that some investigation through drilling of boreholes in the vadose zone near a suspected source had been done and no source was found. As such, this proposal targets drilling into the aquifer and sampling groundwater to identify the head of a groundwater plume, as well as collection of samples from a vadose-zone source area. It may not be possible to optimize borehole locations to meet both of these objectives with a single borehole. There are no specifics as to what the head of a groundwater plume would look like, given data from a few up-gradient boreholes. There is no description of how the investigation will be designed in terms of location of boreholes (how will they be selected?). It will be critical that boreholes are located in the area of highest likelihood of vadose-zone source material to be useful for the PNNL study.

The issue related to significant construction debris near the 183-HR Head House was not addressed, although direct-push technologies were described. I recommend consideration of excavation to the base of the debris and then use of direct-push drilling techniques.

My major review comment relates to timing of the investigation. The recent review panel recommended that additional drilling be conducted **only after** work on a conceptual model for movement of chromium in the vadose zone is constructed through study of a known source area in the 100 B/C Area. The current proposal schedule does not adhere to this recommendation. As proposed, the technical likelihood of the stated-desired outcome is poor. If the schedule is delayed until after building of the conceptual model, it is possible that the technical likelihood of success will be improved.

A deficiency in the proposal is the lack of description of what the samples will be analyzed for. One must assume chromate only. The lack of specific definition of analytes may be result of a lack of understanding of chromium migration and accumulation in the subsurface (i.e., need for conceptual model). This supports the concept of a phased source investigation program, with this work coming later, as described in the previous paragraph. The March 2006 review panel

recommended consideration of other analytes and possible tracer tests that could only be planned after the 100 B/C Area work is completed.
The project fits in well with the overall strategy for the 100-D Area chromium plume by investigating the location of a potential source for the plume, which could then later be treated. The key uncertainty related to this proposal is ability to detect the head of a groundwater plume or a vadose-zone source by drilling and sampling a few boreholes. Presently there is no known signal for a chromium source that could be remotely detected with methods, such as geophysics. Alternatives were considered and the March 2006 review panel recommended drilling *following* construct of a conceptual model to enable better targeting of drilling locations.

I do have a concern that there is no discussion of the investigation in the 100 B/C Area that is supposed to be completed before any drilling in the 100-D Area. Better integration of the entire chromium source investigation program needs to be described. It is awkward that two proposals were received, although I understand that there are two organizations responsible for various activities under the program.

Groundwater monitoring weekly during the entire project is proposed. This may not be necessary and could possibly result in reducing analytical costs that could be applied towards drilling an additional borehole or for another activity. I recommend monthly sampling for 3 months and then quarterly sampling afterwards. What parameters will be analyzed besides chromium? Dissolved oxygen, nitrate, pH, and conductivity should be analyzed at a minimum.

There is little information about the proposed modeling and statistical study to be completed after the data are received. Perhaps some statistical analysis should be done at the beginning of the project to help plan the seven (or ten?) borehole locations. A conceptual model would enable a better investigation strategy.

Implementation Strategy:
Sequence and timing of activities is currently **not** appropriate, as the review panel recommended that the investigation in the 100 B/C Area be conducted first, so that a conceptual model for movement and accumulation of chromium in the vadose zone could be built and utilized to help guide drilling locations and sampling strategy to locate the source in 100-D Area.

The budget and level of effort is reasonable, although no detail was provided.

Proposed Performance Metrics:

There is no information in the proposal about performance metrics. It appears that location of the head of the chromium groundwater plume and the source in the vadose zone are goals, but no groundwater or soil chromium concentrations were identified as being definitive of these goals. There is no description of what the head of the plume would look like in map view or what a vadose zone source area would look like in terms of soil concentrations. This further illustrates the need for the conceptual model based upon data from a known source area. This conceptual model is needed so that when boreholes are drilled and samples collected, appropriate analytical measurements will be made.

Summary Evaluation:
In summary, the proposal addresses a valid technical need to supplement the Insitu Redox Manipulation Barrier through investigation of the location of a potential chromium source up-gradient of the barrier. I recommend that the work be conducted, **but only after** the investigation in the 100 B/C Area is completed and a conceptual model for migration of chromium in the vadose zone is developed. The conceptual model is needed to understand where (horizontally and vertically) and what (what analytical parameters will be measured) to sample and analyze as cores are collected during drilling. Better integration of the 100 B/C Area chromium source area investigation as input to this work needs to be described in the proposal.

Reviewer # 3

Target Plume/Area: 100D Area

Proposal Title: Refine Location of the Chromium Source at the 100D Area and Support a Geochemical/Mineralogical Study of Chromium in the Vadose Zone

Technical Basis of the Proposal:
Is the project or activity based on appropriate and valid science?
Yes. Proposed work involves the use of small-diameter drilling techniques (likely either enhanced access penetration system (EAPS) or hydraulic hammer rig (HHR)) to obtain soil samples from suspected source area for the southwestern 100-D Area chromate plume, and to collect groundwater samples to further refine the location of the plume. This information will be used to further support work proposed in "Chromium Vadose Zone Characterization and Geochemistry," a companion proposal submitted by Pacific Northwest National Laboratory.

What is the technical likelihood of the stated-desired outcome? Fair. Proposed work focuses on drilling of approximately 7 wells near the site of the 183-HR Head House. The technical likelihood of the stated-desired outcome hinges greatly on the effectiveness of these 7 wells to yield useful plume information. Suggest including discussion on why 7 wells were selected, including a discussion on methods employed to optimally locate these 7 wells. Also, expand on periodicity of vadose zone sampling, and how this ties-in to improving conceptual model for source plume in 100-D Area.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? This effort represents an integral component of an overall systems-based approach to remediate the chromium plume in the 100D area. Specifically, this effort is geared towards refining the location of the chromium source plume through small-diameter wells, and soil and groundwater sampling. Additional projects include (i) reinforcing (or repairing to some degree) an existing insitu redox manipulation (ISRM) barrier placed in the 100D Area in 1999; (ii) immobilization of chromium in the ISRM plume by circulating a strong reductant in the aquifer; (iii) enhancing the current pump and treat effort by replacing the ion exchange treatment method with electrocoagulation; (iv) remediation of waste sites along the Columbia by 2012 through the River Corridor; and (v) advanced geochemical characterization of Cr(VI) leaching/retention in Hanford 100 B/C/D Areas. This suite of proposed activities is oriented towards generating a reduction environment. While good, this proposal would again greatly benefit from direct comparison with alternative methods regarding technical feasibility, especially cost.

Is the proposed approach reasonable and practicable?
Yes, although this reviewer has significant concern with the lack of detail and statement of performance objectives in this proposed effort (similar concern was raised regarding an earlier submission). For example, Task 2 Work Plan notes that the "Work Plan will detail objectives and performance criteria for the work as well as scope and schedule." While the work schedule and proposed activities are detailed in nature, specific objectives and performance criteria are

rather ill-defined. Further, the total project costs of approximately $650,000 appears rather high for costs for 7 small-diameter wells and associated sampling and monitoring (the stated costs are based on prior well-drilling sampling, and groundwater monitoring operations, but are the well-drilling costs representative of costs for small-diameter wells?). Further, approximately $95,000 is earmarked from preparation and review of an evaluation report for this effort – is this effort/cost justified?

What are the risks or key uncertainties in the proposed action(s)?
Risks/uncertainties primarily relate to the ability of the selected 7 wells to locate the chromium source in the saturated zone and/or the vadose zone. Previous submission reviews suggested the use of low-frequency ground-penetrating radar (GPR), ground conductivity meter (GCM), or magnetic surveys to assist in locating large boulders that could then possibly be avoided during the drilling activity. Other than "comment noted", this reviewer does not see any evidence that GPR or GCM would be employed to further assist in locating the 7 wells.

Are there clear examples of alternative ideas or proposals that should be considered?
Yes -- use of existing plume and geology information coupled with forensic modeling. Proposal lacks detail on how existing information will be effectively employed to further refine location of the source plume. Further, the proposal did not address specific objectives on modeling efforts. For example, statements such as "modeling will use the groundwater chromium data, coupled with analysis of groundwater flow in the area, to refine a conceptual model for chromium in the vadose zone and groundwater" insufficiently describe modeling objectives, methodologies, and performance measures.

Implementation Strategy:
Is the sequence and timing of activities appropriate?
Yes, although additional "preliminary" effort should be made to make use of existing plume and geology information coupled with forensic modeling.

Can the technology be implemented cost-effectively?
Maybe. Use of GPR and GCM should be explored as a means to further refine the planned location of the 7 wells. Further, suggest using information obtained from drilled wells to locate subsequent wells.

Is the budget and level of effort appropriate for the proposed work?
No. Lack of sufficient detail on budgeted items (e.g., $385k for small-diameter well drilling and $95k for report preparation and review).

Proposed Performance Metrics:
Does the proposed project or activity represent a significant improvement compared to the baseline?
Yes. The current baseline technology employed conventional drilling and trenching, coupled with groundwater monitoring and excavation of near-surface waste sites.

Use of geophysical techniques (and/or EAPS) coupled with appropriate modeling may greatly enhance the ability to locate the source of the chromium plume.
Does the project improve the protection of the Columbia River now or in the future?
Yes, success of this effort (i.e., location of the source plumes) can assistance in reducing the time, expense, and potential for migration of the chromium plume to the Columbia River in the future.

Are there measurable parameters that would document performance? Not specifically stated in the proposal. Stated performance objectives should include: (i) criteria for selection of location of 7 wells (e.g., performance matrix to guide decision of panel on most suitable well location based on several criteria); (ii) decision support to identify best small-diameter well technology to be employed (and related performance measures for that method); and (iii) clear articulation of what defines "success" in terms of plume location refinement.

Are these included in the proposal?
No – at least not in sufficient detail to discriminate success or failure.

Summary Evaluation: In general, the ideas put forward with this proposal are a nice improvement over the previous proposal to employ geophysical techniques to further refine the location of the chromium source in the 100-D Area. Strengths include (i) targeting the sources of the chromium plume(s); (ii) employment of less-expensive and likely more successful (in terms of ability to penetrate 100-D Area strata) small-diameter drilling technologies; (iii) collection of soil and groundwater samples to further quantify potential source plume location; and (iv) tie-in with both previously proposed and currently proposed chromium source plume refinement activities in terms of a system-based effort to provide estimates of source locations. Concerns include (i) lack of sufficient detail/technical support for justification/selection of 7 wells; (ii) lack of detail in employment/potential use of historical geologic, soil sample, and groundwater monitoring information, including estimates of backward location and travel time probability distributions for the observed contamination; (iii) lack of mention of use of GPR/CMT to assist in well location; and (iv) little to no detail on performance metrics (e.g., what criteria will be employed to guide the location of the 7 wells?; what will define failure or success for well drilling, sampling, and monitoring?).

Reviewer # 4

Target Plume/Area: 100-D Area Chromium Plume

Proposal Title: Refine Location of the Chromium Source at the 100-D Area and Support a Geochemical/Mineralogical Study of Chromium in the Vadose Zone

Technical Basis of the Proposal:
The proposal is based upon valid and appropriate science. The general strategy of moving upgradient (in the groundwater) to bracket the potential location of the source in the vadose zone or shallow groundwater is sound but is subject to significant technical uncertainty in a real world setting with heterogeneous geology and with a variety of possible release locations – the plume is not a well behaved set of ovals, especially near the potentially disparate source release, migration and accumulation locations. The proposed work, while generally well conceived, would benefit from better integration with the conceptual model development in the related geochemistry proposal, as well as with ongoing activities (such as the excavation and removal of the chromate transfer lines).

The selection of the drilling technology appears reasonable and is justified in this shallow but challenging setting. The plans should allow for refusal and have a strategy for how alternate locations are selected for additional penetration attempts.

A more complete listing of analytes is needed as well as the logic and justification. I would encourage the investigators to carefully select, test and implement their methods to make sure that the measurements of Cr(VI) versus other oxidation states are accurate under the range of expected site specific conditions (e.g., impacts of carbonates, etc.). This is another opportunity to collaborate with the geochemists to minimize the risk of inconsistencies.

Task 2 is the time during which drilling locations are selected. While this is realistic, the proposal does not provide sufficient information on the process that will be used to select the locations (What are the parameters to be considered and balanced? What are the data sources? How does the selection process beneficially use and integrate the available historical data, data from current removal actions, and data from the related geochemistry study in 100 B/C?). I recommend that the selection strategy be developed as part of implementing this work. This integration might be extended by considering sampling during any ongoing removal actions – this might provide direct access to highly contaminated sediments and the ability to opportunistically extend samples down several meters using hand coring techniques in environments where obstructions are not encountered. Because the source remediation contractor is likely limited in their scope to gross analysis of chromium, the supplemental funding would provide a real opportunity for measuring additional parameters that would provide key data for refining the source location.

Weekly groundwater sampling may not be necessary – weekly sampling should be discontinued after concentrations recover from the installation trauma and stabilize and then a longer timeframe employed (e.g., monthly or even quarterly). This project has minimal need for hourly groundwater level data and automated logging/access and the proposal should not describe such a system as an integral part of refining the chromium source location.

Implementation Strategy:
This project needs to be better integrated into the related supplemental research and baseline activities.

The overall budget and level of effort is a bit high and there is little documentation of the need for $95K for planning. While the overall cost of $650K is high for only 7 boreholes, this work also includes analysis of many samples, conceptual model development and many other elements – the budget should be reviewed for reasonableness.

Proposed Performance Metrics:
While the proposed work is generally reasonable and appropriate, performance metrics are missing -- these should be developed as part of the implementation and work planning with DOE based on the technical and implementation comments above.

Summary Evaluation:
The proposal addresses a valid technical need. I recommend that the work be conducted, but better integration of the 100 B/C Area chromium source area investigation as input to this work needs to be described in the proposal.

APPENDIX F

Initial Calcium Polysulfide Test for Accelerated Clean Up of the Southwestern Chromium Plume in the 100-D Area

Target Plume /Area: Chromium (Cr(VI)) / Hanford 100-D Area

Proposal Title: Initial Calcium Polysulfide Test for Accelerated Clean Up of the Southwestern Chromium Plume in the 100-D Area

Proposal Reviewers: Brian Looney, Todd Anderson, David Cocke, Miles Denham, Mark Fuhrmann, Dawn Kaback, Gene LeBoeuf, and Bruce Wielinga.

Summary Evaluation:
The panel does not support the proposal as written; however, the panel does support the concept of upgradient treatment to augment the performance of the ISRM barrier. Although calcium polysulfide (CPS) will effectively reduce upgradient Cr(VI) contamination to Cr(III), the panel believes there are alternatives that are likely to be better suited to the upgradient (of the ISRM barrier) treatment of the Cr plume. These alternatives should be evaluated, in terms of costs and ease of implementation and longevity, to determine their relative effectiveness in comparison to CPS. The panel provides a significant number of recommendations that should be considered. The proposal should be rewritten for a second peer review.

Technical Basis of the Proposal:
The panel believes a proposal to chemically reduce Cr(VI) to Cr(III), as well as the flux of other oxidants to the ISRM barrier, is based on valid and appropriate science, and fits well with the integrated systems approach to accelerate the cleanup of Cr(VI) contamination near the Columbia River. Such a strategy supports a "defense in depth" environmental management strategy, which was recommended by the National Academies-National Research Council. Use of CPS to achieve this goal is potentially viable, but the panel believes that alternative reductants and electron donors are likely to be better choices – i.e., less aggressive and toxic when applied and providing a longer period of chromium conversion and oxygen and nitrate scavenging.

General technical issues for consideration:

- The proposal did not adequately describe where the injections would take place, at what depth, and in what ways one would expect CPS to be better than alternatives – the selection of CPS was not justified. An alternatives analysis that is linked to the 100-D Area conceptual model and linked to the 100-D Area systems approach for protecting the Columbia River is required to move this strategy forward. (see reviewers 2, 4, 5, 6, 7, and 8)

- Demonstrate how the proposed number of injection wells was determined and if it is appropriate.

- Consider the impacts of subsurface heterogeneity on the delivery and transport of CPS. The proposal does not provide an adequate explanation for how CPS will be delivered.

- Consider the impacts of CPS toxicity and other geochemical interactions on the aquifer geochemistry and microbial populations therein. Also, the impacts of the byproduct formation and increase in pH on the downgradient Columbia River should be considered – there is a need to balance the potential impacts of higher pH and other perturbed chemistry versus ppb levels of Cr(VI) on salmon breeding zones. (see reviewers 1, 3, 7, and 8)

- CPS and zero-valent iron (ZVI) are not compatible, so injecting CPS too closely to the ISRM barrier could impact its effectiveness. (see reviewer 2)

- Address the impacts of CPS on the geochemistry of the subsurface, groundwater, and river (see reviewers 1, 2, 3, 6, 7, and 8):
  - CPS could release significant amounts of sulfur in the subsurface that could be oxidized by soil bacteria to form sulfuric acid, which lowers soil pH. Given the potential of the ISRM barrier to raise pH, this acidification may be beneficial overall, but the potential long-term effects of adding large amounts of sulfur to the aquifer should be carefully considered. Also, the possibility of CPS to produce sulfate could impact the effectiveness of the downgradient ISRM barrier and the proposed electrocoagulation treatment system for the proposed expansion of the pump and treat system by plugging pores.
  - Consider the impacts of introducing a significant amount of calcium into a system that may be naturally saturated with calcite.
  - Safety, process, and handling issues need to be better considered for CPS. For example, CPS reacts explosively with strong acid to form hydrogen sulfide.
  - CPS could cause the mobilization of naturally occurring arsenic and other trace elements.
  - The high pH of CPS could disperse clays and initially mobilize chromate.
  - The high pH and low Eh of CPS will alter the aquifer geochemistry – the effects of shifts in these controlling “master variables” on the major and trace elements, including contaminants, should be generally evaluated.
  - Consider the quality of the groundwater after treatment and its compatibility with the downgradient ISRM barrier.

- Address the concern that using this technology to create an upgradient treatment zone is somewhat redundant with the ISRM barrier, if the same objectives are set for each process. The upgradient treatment objectives need to be set to be consistent with the role of the process in the overall systems approach. The upgradient treatment could be targeted to reduce oxygen and nitrate in the groundwater, so that when the groundwater reaches the ISRM barrier, treatment can focus on reduction of chromate.

- It might be more appropriate to use CPS to address the contamination source or areas of high contamination, rather than to be deployed broadly across a dispersed plume. It might be "too big a hammer" to use for existing concentrations of chromium. Evaluate less aggressive, more benign reductant alternatives.

- Consider that CPS is a relatively new technology that has not been well tested.

- Evaluate alternatives to CPS using a consistent unit for comparison (e.g., based on electron donor potential and the profile of the impacts through time). Reductant alternatives to CPS include (see reviewers 1, 2, 4, 5, 6, 7, and 8):
  - Various organic reductants (e.g., lactate, carbohydrates like molasses or corn syrup, vegetable oil or emulsified vegetable oil, proprietary products like HRC Advanced, etc.) with potential to remove chromate from the groundwater. In addition to removing chromate, organic reductant would also remove oxygen and nitrate, reduce the amount of precipitated sulfur, and be safer and significantly cheaper than CPS.
  - Inorganic reductants (e.g., iron sulfates, sodium dithionite, etc.)
  - A combination of organic nutrient reductant and CPS.

- Consider pump and treat.
-

Implementation Strategy:

- The panel generally supports the proposed sequencing and timing. Implementing reductant injection should be strongly coordinated with the other projects in the integrated systems approach.

- Injecting an upgradient treatment might be better delayed until results of the ISRM barrier mending with ZVI are complete and the alternatives evaluation is completed and peer reviewed.

- Consider a dipole deployment (i.e., a combination of injection and extraction).

- The proposal provides little description of costs associated with implementation, such as the location of wells, operating costs, etc. A significant portion of the project is allocated for installation of wells. Consider alternatives. Infiltration galleries should be considered as an alternative.

- The proposal should include a more detailed discussion of budget costs. Consider the relatively high costs of applying CPS over a large area.

- Consider orienting the treatment parallel to flow, through the middle of the plume to treat as much chromium as possible. (This concept would need to be performed as an injection/extraction system to avoid spreading the plume.)

- Consider potential stakeholder concern that this technology does not address the source of chromium contamination. Stakeholders might be more amenable to using CPS if the sources of chromium contamination were known and the highest concentrations were targeted with such an aggressive reagent.

- Consider that injecting CPS may be too aggressive as an upgradient treatment to augment the ISRM barrier. The ISRM barrier, which is proposed for mending, provides an effective treatment and the reductant should be designed to be cost effective and safe while recognizing that the action is part of the systems approach.

- The proposal needs to provide a better and more detailed description of the pilot field test; however, a pilot test may not be necessary considering one was completed in the Hanford 100-K Area.

- Perform a cost estimate for a full-scale implementation of the CPS injection project to determine its cost-effectiveness.

Proposed Performance Metrics:

- Although the panel generally agreed with the proposed performance metrics, additional performance metrics should be described in detail and integration with the ISRM performance metrics (including ZVI injection) should be done. Concern regarding generation of byproducts may require a tighter monitoring system with wells located close to the injection wells.

- Implement a comprehensive and extensive monitoring program for the injection of CPS to address the potential for collateral impacts to the river.

- Consider monitoring parameters in addition to Cr(VI) concentrations, such as performance reductions, electron capacity, dissolved oxygen, pH, and other indicative and/or potentially harmful parameters. Identify concentrations/levels of these parameters that indicate relative success.

- Employ additional monitoring points close to the point of injection to monitor for byproducts.

Reviewer #1

Target Plume/Area: Chromium/Hanford 100D Area

Proposal Title: Initial Calcium Polysulfide Test for Accelerated Clean Up of the Southwestern Chromium Plume in the 100-D Area

Technical Basis of the Proposal:

Is the project or activity based on appropriate and valid science?

Yes. Polysulfide solutions will definitely produce reducing conditions in the subsurface. Cr(VI) is susceptible to reduction to the insoluble Cr(III) form by a variety of potential reductants including sulfide and Fe(II) both of which will be produced insitu by polysulfide injection.

What is the technical likelihood of the stated-desired outcome?

The intent is to augment the abilities of the reactive barrier already in place in the 100-D area. Polysulfide injection immediately upgradient will certainly provide reducing conditions. The planned laboratory and field experiments should provide some information as to whether soluble Cr(VI) can be reduced to below the EPA MCL. However, just as with the current barrier, heterogeneous groundwater flow and mixing will determine whether this limit is actually reached.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable?

The project is part of a larger program to augment the reactive barrier already in place at the 100-D area. The barrier has not proven to meet expected performance criteria (what were the criteria?) and requires more intervention to augment its Cr(VI) removal capabilities. Sulfide injection to produce a reduced subsurface (Fe(II), S) immediately upgradient will certainly produce reduced conditions and facilitates some removal of Cr(VI) from the groundwater. There is ample thermodynamic and practical data to support this. The polysulfide technology is intended to put into place more reducing power to augment the reactive Fe(II) in the existing barrier.

What are the risks or key uncertainties in the proposed action(s)?

The proposed injected polysulfide solution is a high pH, concentrated liquid amendment. There will need to be some assurance that this solution goes and stays where it is supposed to and is not transported to the Columbia River. Sulfide is toxic, particularly to “higher” organisms (salmon). The injected high pH, polysulfide solution may interact with the redox barrier that is already in place. Will sulfide impact the ZVI amendment? Polysulfide is a highly alkaline solution. The proposed addition of Fe(0) particles to the barrier will also produce a high pH environment. pH needs to be one of the monitoring parameters employed to track performance of the proposed barrier and sulfide injection.

Are there clear examples of alternative ideas or proposals that should be considered? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)
Instead of polysulfide, has Fe(II) injection been considered as an alternative? This is not as reducing as sulfide but would reduce Cr(VI) to Cr(III) without the potentially toxic effects of sulfide. Injection is tricky though.
Was sodium dithionite not considered? Addition of dithionite has already been done at this site once before (ISRM) and dithionite injection would not entail introducing a "new" chemical (toxic) species into the subsurface at this site.

Implementation Strategy:
Polysulfide solutions are commercially available (locally). The budget appears to be appropriate for the level of effort proposed.

Proposed Performance Metrics:
What are the metrics…zero Cr(VI) transport to the river, lowered Cr(VI) transport to the river? The metrics need to be carefully defined.
There was some discussion of metrics in the proposal but I would like to re-iterate that a meaningful monitoring program needs to be put into place to address the potential for sulfide transport to the river. What is the plan if detectable sulfide concentrations appear in monitoring wells close to or in the river and what appropriate action will be taken? If the pH of groundwater remains very high through the barrier and into the riparian zone /river, what is the appropriate response to this potential event? Are we concerned about alkaline, potentially sulfidic water entering the Columbia River or just Cr(VI) entering the river? If Cr(VI) concentrations are below the MCL for the site but sulfide and high pH water is entering the river, what has been accomplished and at what cost to the environment? These are questions that need to be addressed in the proposal.

Summary Evaluation:
Injection of polysulfide into the 100-D aquifer immediately upgradient of the ISRM barrier will certainly produce reducing conditions in this vicinity. Cr(VI) is likely to be reduced to Cr(III) when contacted by sulfide and/or Fe(II), but much depends on placement of the injected solutions into the right position in the subsurface. Similar to the barrier already in place, groundwater flow heterogeneities and mixing issues upon injection will govern the successful reduction of Cr(VI).
How will the polysulfide sulfide solution be tracked in the subsurface? Can SP be used? This is critical because sulfide is toxic and will impact the riparian zone and the river if transported that far in the subsurface. Also, the issue of injecting/producing extremely high pH solutions in the subsurface will need to carefully monitored. High pH is not conducive to healthy riverbanks or salmon spawning grounds either. Are there no other, less toxic reductants that could be used in this instance? I favor the use of this technology only for exceptionally concentrated source areas.

I cannot recommend that this technique be adopted for widespread to treat the plumes at the site. There are other alternative, less toxic solutions to produce reducing conditions within the plumes. Bioreduction is one option that was discussed by the panel. Cr(VI) bioreduction works well and a demonstration of this technique is currently being tested at the Hanford site.

Reviewer #2

Target Plume/Area: Hanford Site, 100-D Area

Proposal Title: Initial Calcium Polysulfide Test for Accelerated Clean Up of the Southwestern Chromium Plume in the 100-D Area

Technical Basis of the Proposal:
Is the project or activity based on appropriate and valid science?

The science is appropriate and valid. It fits well with the overall integrated systems approach of being an insitu chemical reduction procedure. The project seeks to treat the chromium contaminated plumes and the best practice science usually uses one of the following:

Sodium Dithionate ($Na_2S_2O_4$)
Calcium Polysulfide (CaS_x)
Ferrous Sulfate ($FeSO_4$)
Enhanced bioremediation (adding organics to plume)

In addition the objectives of this proposal go beyond the chemical reduction of Cr(VI) to Cr(III). The deployment of CPS is proposed to serve two major objectives in the overall cleanup strategy of this plume. The first objective is to extend the longevity of the ISRM barrier by creating an up-gradient treatment zone that reduces the oxidative capacity and thus reduces the oxidation rate of the barrier. The second objective is to reduce the mass and size of the chromium plume, particularly the high concentration areas, by deploying the CPS technology directly to the plume.

The chemistry supporting the CPS addition is appropriate and sound. It should provide the means to meet the two above objectives. This is supported by the reducing capacity of CPS and the insolubility of the products. The latter has recently been reconfirmed for sulfides over a wide range of pH. (J. Envir. Eng., Volume 128, Issue 7, pp. 612-623 (July 2002)).

Calcium polysulfide precipitates metals as less soluble and non-toxic sulfides and hydroxides as well as reduces Cr(VI) to Cr(III), which possibly then precipitates as chromium hydroxide and/or as iron chromium hydroxide [$Cr_xFe_{1-x}(OH)_3$] with substantially lower solubility than pure chromium hydroxide. The generalized equation describes the overall process:

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

where it can be seen that elemental sulfur is also produced.

This is further supported by the successful treatability test using CPS technology performed in the 100-KR-4 area in 2005.

However some attention needs to be paid to the possibility that Calcium Polysulfide injection into ground water is suspected of producing large amounts of sulfate. This can have several effects: sulfate precipitation can plug pores, sulfate might reduce the effectiveness of injected zero valent iron (Permeable Reactive Barrier (PRB) using zero valent iron (ZVI) injected to mend existing barrier) by interfacial passivation and the sulfate may interfere with electrocoagulation unless appropriate counter measures are taken during the EC.

What is the technical likelihood of the stated-desired outcome?

There is considerable technical likelihood of the stated-desired outcome as evidenced by the successful treatability test using CPS technology performed in the 100-KR-4 area in 2005.

How does the project fit in with the totality of proposed activities for the target contaminant/plume?

The application of CPS technology fits well with the totality of the proposed activities for the target chromium and the plume(s) identified in the 100 D area. The refinement of the location of the Chromium Source in the 100 Areas is appropriate for the application of the CPS technology since it can be directly applied to the most problematic plume areas as well as be used to generally reduce the oxidative capacity and Cr(VI) concentration u-gradient of the ISRM The application of Calcium Polysulfide is also quite compatible with EC technology if the additional sulfate that results can be effectively handled. Both CPS and EC are chemically related since the goals of the two technologies are to ultimately chemically reduce the Cr(VI) to Cr(III). However, it is yet to be determined if the additional species introduced into the plume water will interfere with the EC process or in the efficiency of the ZVI that is planned.

The project to immobilize mass in the ISRM plume by circulating the CPS, a strong reductant in the aquifer should also create a persistent zone of reduction that will continue to treat chromium under natural groundwater flow conditions. EM-21 Proposal.

Is the proposed approach reasonable and practicable?

The new, integrated approach to accelerate cleanup of chromium in the 100 Areas is absolutely the most reasonable and practicable approach. The integrated approach of using an insitu reductant, building more robustness in the ISRM's and using a chemically complementary technology of EC is excellent. Again, there is a need to explore the synergistic aspects of the three approaches as well as the interferences such a surface passivation of the zero valent iron by sulfides and sulfates as well as the interferences in the EC process that might result from the insitu processes. In addition, there needs to be a comparison of the CPS approach against the following:

Sodium Dithionate ($Na_2S_2O_4$) (apparently not being considered)
Ferrous Sulfate ($FeSO_4$)
Enhanced bioremediation (adding organics to plume)

Where the latter needs a closer look.

What are the risks or key uncertainties in the proposed action(s)?

Given the successful treatability test using CPS technology performed in the 100-KR-4 area in 2005 and the lack of noted unexpected consequences there seems to be no obvious risks or key uncertainties. However, it is again recommended that the three processes be examined for both synergisms and interferences.

In addition, given the complexity of the system and since the recommendations for determining the products, speciation and stability of reduced Cr in the plume zone, 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 are in some cases intractable and go beyond the capacity of the current proposals there will be some uncertainties associated with the project that will have to be determined in the field testing. The suggested field testing was also extensive and was proposed to have: 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 insitu rates of reduction and capacity, and 4) monitoring for performance and potential loss of reductant. Including some of this type of testing of CPS would assure a minimum of uncertainties.
Numerous species (Ca, Fe, Mg, Mn, Al, Ba, Cl, F, CO_3^{2-}, SO_4^{2-}) may affect precipitate formation in CPS and Sodium Dithionate application in reactive barriers and these species sometimes coat reactive surface areas and consequently decrease reactivity and lower permeability by clogging pore spaces, which generally results in a shorter lifespan of the barrier. (U.S. Environmental Protection Agency (USEPA). September 1998. Permeable Reactive Barrier Technologies for Contaminant Remediation. http://clu-in.org/download/ rtdf/prb/reactbar.pdf).

Are there clear examples of alternative ideas or proposals that should be considered?

The most important ones have already been considered in the TECHNICAL ASSISTANCE PROJECT #33

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

However , the enhanced bioremediation process with organics injection needs to be carefully examined.

With the CPS and microscale iron being chosen for further work the proposed project is appropriate but needs to be examined against enhanced bioremediation.. So the answer is yes, the reasoning given for the choice of the Ca Polysulfide in report “Evaluation of Amendments for Mending the ISRM barrier, Technical Assistance Project #33, Final Technical Solutions Report, DOE” are sound but organic injection is a possibility that also needs to be examined.

Implementation Strategy:
Is the sequence and timing of activities appropriate?

Yes, the sequence is appropriate to the scale and scope or the project. However, the sequence needs to be carefully timed with the other projects including the geophysics examination for refined location of the Cr source.

The summary implementation schedule provided in Figure 5 assumes that the authorization to proceed is given prior to April 1, 2006 and that any HQ peer review is also completed before April 1, 2006. However, this must be strongly coordinated with the other projects.

Can the technology be implemented cost-effectively?

Yes, the cost of CPS is competitive with the most cost effective chromium treatment technology available. However, the cost and benefits of bioenhancement needs to be looked over carefully as an alternative.

Is the budget and level of effort appropriate for the proposed work?

Yes.

Proposed Performance Metrics:
(Does the proposed project or activity represent a significant improvement compared to the baseline? Does the project improve the protection of the Columbia River now or in the future? Are there measurable parameters that would document performance? Are these included in the proposal?)

Does the proposed project or activity represent a significant improvement compared to the baseline?

The existing baseline technology for the southwestern portion of the 100-D plume is ISRM (produced by Sodium Dithionite injection), which is the preferred alternative as defined in the 1999 amended 100-HR-3 interim action ROD. The proposed activity represents a significant improvement compared to the above baseline.

Does the project improve the protection of the Columbia River now or in the future?

Yes, the project improves the protection of the Columbia River.

Are there measurable parameters that would document performance?
Yes, these have been identified in the risks and key uncertainties section.

Summary Evaluation:
The proposed work of treating the plume at some distance up-gradient from the barrier is a very good approach. However, the interferences and complications when combined with the ZVI repair of the barrier needs to be evaluate. This brings to fore an alternative approach of organics injection for enhanced bioremediation. This needs to be carefully considered. The plume treatment should also be considered as a tool to help locate the Cr source by minimization of the area of the plume. The approach is however a good next step toward the protection of the Columbia River and should be taken. Other options need to be considered.

Reviewer #3

Target Plume/Area: 100-D Area Uranium Plume

Proposal Title: Initial Calcium Polysulfide Test for Accelerated Clean Up of the Southwestern Chromium Plume in the 100-D Area

Technical Basis of the Proposal:
Calcium polysulfide will successfully reduce chromate, but so will any number of other less vigorous approaches.

If chromate sources are spatially related to the presence of carbonate in soils, then using a calcium salt may not be appropriate. This relationship could indicate that chromate is preferentially bound in carbonate minerals or as the mineral chromatite ($CaCrO_4$). If this is the case then addition of calcium could cause additional precipitation of these phases resulting in creation of slowly dissolving chromate sources.

Possible collateral damage of using calcium polysulfide:

- dispersal of clays by high pH
- initial mobilization of chromate by high pH
- does dissolution of ferric iron phases release any sorbed contaminants?

Implementation Strategy:
Implementation strategy looks okay. Budget seems high ($1.2 million). I'm not sure I would say calcium polysulfide is easy to handle – corrosive, H2S hazard if contacts acid, etc.

Proposed Performance Metrics:

Summary Evaluation:
A viable way to reduce chromate in the subsurface, but there may be other equally viable options. Budget seems high.

Reviewer #4

Target Plume/Area: 100-D Area Cr plume

Proposal Title: Initial Calcium polysulfide test for accelerated clean up of the SW Cr plume

Technical Basis of the Proposal:
The technical basis of this project is the use of calcium polysulfide in place of sodium dithionite as a reducing agent that is injected into the subsurface to precipitate high concentration Cr(VI). As some failures in the original treatment wall have been noted, the approach has been modified to use this material upstream of the treatment wall to immobilize Cr closer to the source, making the current treatment wall a secondary barrier.

Little information was provided in the proposal regarding details of where the injections would take place, at what depth, and in what ways one would expect the new reagent to be better than the original one. The basic idea of adjusting the plan to immobilize the higher concentration Cr (VI) is appropriate given that portions of the original wall are unable to remediate the high concentrations they are challenged with. The project is reasonable and practicable as it is part of a larger effort to find the sources of Cr, move up-stream to get at high concentrations of contaminants, and repair the current treatment wall, although other methods of achieving reduction in the saturated zone should be examined, especially for cost. Care should be taken that the polysulfide treatment does not hinder the reactive wall behavior, by altering groundwater chemistry.

The use of the polysulfide may be more appropriate to high concentration source areas than to the dispersed plume. This is especially so because of concerns about adverse water quality due to the sulfide. The chemistry of Cr in the source areas, if they are located, may be very different than assumed since reactions between the very concentrated sodium dichromate and the soil probably resulted in a variety of reaction products. The method of assessing Cr in the soil, by only doing analysis for Cr(VI) is not adequate….total Cr is needed too…..Once Cr(III) is generated it apparently tends not to go back to Cr(VI). However, in a concentrated source area, with unknown reactions there may be enough disproportionation that Cr (VI) will bleed out over time and supply the plume.

The TAT recommended that a carbon source be included with the polysulfide. Why was this not considered here?

Implementation Strategy:
The sequence and timing seem OK. Cost seems reasonable for this proposal. Essentially no details were given regarding well locations, reagent volumes, estimated size of treatment zones, making judgment difficult.

Proposed Performance Metrics:
The baseline is the ISRM which although it was estimated to last for 20 years based on lab studies, portions of it failed in 10% of that time. This project will reduce concentrations of aqueous Cr impacting the ISRM. As such it will be an improvement of the baseline. The performance metric is reduction of Cr(VI) to obtain groundwater concentrations of less than 20 ppb. I suggest another to define a target of some lifetime of the treatment zone: 5 years or 10 years.

Summary Evaluation:
This project is sound and is an expansion of existing treatments to adjust to problems with the original approach. It is however, limited by the state-of-the-art. The reasons for changing to a different reagent is not documented, but it has been used in similar applications. Other means of providing Cr reducing conditions in the dispersed plume may be more cost effective and less problematic for water quality than the polysulfide, and additional benefit of reducing nitrate concentrations by carbon source addition should be one of the considered options.

Reviewer #5

Target Plume/Area: 100 Area

Proposal Title: Initial Calcium Polysulfide Test for Accelerated Cleanup of the Southwestern Chromium Plume in the 100-D Area

Technical Basis of the Proposal:

1. The project is based on appropriate and valid science, as calcium polysulfide has been demonstrated to reduce chromium in the field; some issues exist related to delivery (related to heterogeneity), long-term effectiveness, and cost; recommendation of calcium polysulfide as a reductant to treat chromium was made by an expert panel in 2004. A pilot test was recently completed in the 100-K Area. This particular proposal involves use of the material as an upgradient treatment. There is not a lot of specific material about the details of the proposed field test; the proposal needs to be rewritten with more detail. *They are planning two injection wells and one extraction well.* The need for this aggressive treatment as an augmentation of the barrier is questioned. I don't recommend this approach, but instead recommend the ZVI mending of the barrier itself and a more gentle upgradient treatment that primarily targets removal of oxygen and nitrate, so that chromium removal can occur at the ISRM.
2. There is concern about interaction of polysulfide and downgradient ZVI.
3. The likelihood of the desired outcome is good, but issues described above could impact performance and there are questions about the cost, due to the large size of the plume to be treated.
4. The approach is not reasonable. The strategy of an upgradient treatment zone was proposed by the expert panel in 2004. However, the selection of the treatment reagent is not reasonable, as it proposes to basically replace the downgradient ISRM, which is proposed for mending. There is likely a lower cost alternative.
5. Key risks and uncertainties relate to the delivery, long-term effectiveness, and cost of treatment.
6. Alternatives that were examined for mending of the downgradient ISRM barrier (two 2004 expert panel reviews) included zero-valent iron, re-injection of dithionite, bioremediation upgradient to remove the co-contaminants (oxygen and nitrate which utilize the bulk of the reductant).
7. Alternatives for the upgradient treatment to target removal of oxygen and nitrate that should be considered include: lactate or other organic reductant (much more effective on a per mole basis as compared to calcium polysulfide, much cheaper, and much safer.
8. Fluor should do a cost estimate for a full-scale implementation. A cost estimate comparing calcium polysulfide and an organic reductant was done in the 2004 Technical Assistance Report. The calcium polysulfide may be overkill and may cause some issues with downgradient interactions with the ISRM.

Implementation Strategy:
- Sequence and timing of implementation of an upgradient treatment may be appropriate, although it could be put on hold until the results of the barrier mending with ZVI is done. However, the upgradient treatment provides "defense in depth."
- Consider deploying parallel to flow and not perpendicular.
- If the project is conducted, significant work to understand subsurface heterogeneity needs to be conducted prior to design of an injection scheme for the calcium polysulfide. Is the plan to inject the fluid throughout the aquifer thickness equally, as was done for the ISRM? Heterogeneity may be a problem with this approach.
- There is not much detail on the budget in the proposal. Why do new injection wells have to be drilled? Can they use an existing well? I would think some inexpensive monitoring wells would have to be installed though. Vibracore might be the best method for monitoring wells.

Proposed Performance Metrics:
- The project has potential to significantly improve conditions at the ISRM, by treating upgradient. In some ways, it eliminates the need for the ISRM.
- The project attempts to protect the Columbia River by removing significant mass in the plume.
- Effectiveness of CPS does not need to be tested, as a pilot was done in the 100-K Area.
- I don't see the connection with the river environment and the upgradient source to be treated by the calcium polysulfide. I don't recommend that this modeling task be conducted. By the time the groundwater reaches the river environment dissolved oxygen should be back to normal.
- Performance of the technology will be measured by the current monitoring system, but additional monitoring points should be installed close to the injection points to monitor for byproducts, as was recommended in the ISRM mending comment sheet. There is little information about performance monitoring.

Summary Evaluation:
Overall, recommend this technology not be implemented, as written. Calcium polysulfide might be appropriate for source removal, but not for broad application in a large plume. I feel like this technology will basically replace the ISRM rather than being a supplemental upgradient technique to knock out oxygen and nitrate. I support evaluation of lower cost alternatives that might include some type of insitu bioremediation applied through a low-cost, safer infiltration system in the vadose zone. There is also concern about chemical interactions between this technology upgradient and the ISRM. I would like to see a cost estimate of what this would cost for the full-scale application. There is little need to do a pilot demonstration of this technology, as it has already been done in the 100-K Area. We have concerns about extreme chemistry and safety (can generate H_2S). It's a big hammer that isn't needed here. Our federal tax dollars should be spent on a smarter approach.

Reviewer #6

Target Plume/Area: 100D Area

Proposal Title: Initial Calcium Polysulfide Test for Accelerated Clean Up of the Southwestern Chromium Plume in the 100-D Area

Technical Basis of the Proposal:
Is the project or activity based on appropriate and valid science?
Yes. Use of calcium polysulfide to enhance redox barriers in subsurface environments is relatively well-established. The deployment of CPS will serve two major objectives in the overall cleanup strategy of this plume: (i) extend the longevity of the ISRM barrier by creating an upgradient treatment zone to reduce the oxidation rate of the barrier; and (ii) reduce the mass and size of the chromium plume.

What is the technical likelihood of the stated-desired outcome? Good. Numerous applications of this technology have demonstrated that it successfully fixes metal contaminants (e.g. arsenic, lead, copper, cadmium) in the groundwater and vadose zone, including evaluations in the 100-KR-4 Area. Concerns remain, however, regarding targeted injection/extraction sites considering heterogeneity of the subsurface in the 100D area, locating the chromium plume, the likelihood of maintaining reducing conditions over extended time periods, and last, but certainly not least, the cost associated with a full scale-up application for a broad area.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? This effort represents an integral component of an overall systems-based approach to remediate the chromium plume in the 100D area. Specifically, this effort is geared towards immobilization of chromium in the ISRM plume by circulating a strong reductant, calcium polysulfide, in the aquifer. This may also create a persistent zone of reduction that may continue to treat chromium under natural groundwater flow conditions. Additional projects include (i) reinforcing (or repairing to some degree) an existing insitu redox manipulation (ISRM) barrier placed in the 100D area in 1999; (ii) deployment of an electrocoagulation treatment system as part of an expanded pump and treat system; (iii) location of the chromium sources in the 100D Area; and (iv) remediation of waste sites along the Columbia by 2012 through the River Corridor. This suite of proposed activities is oriented towards generating a reduction environment. While good, this proposal and each of the other three chromium-plume related proposals, would greatly benefit from direct comparison with alternative methods regarding technical feasibility and especially cost.

Is the proposed approach reasonable and practicable?
Yes, although again this reviewer has concern regarding the employment of this "strong-arm" method as a broad-based application.

What are the risks or key uncertainties in the proposed action(s)?

Risks/uncertainties include: (i) is the conceptual model for chromium plume in the 100D area correct?; (ii) site heterogeneity causing difficulty in locating and injecting calcium polysulfide solution in correct locations; (iii) longevity of injection (how long will an injection last once the re-circulating system is turned off?; (iv) potential mobilization of naturally-occurring arsenic; and (v) are the proposed number of wells sufficient to meet project objectives?.

Are there clear examples of alternative ideas or proposals that should be considered?
Yes. Pump and treat has been very successful in the 100K area. Further, what about the employment of other reduction techniques in depth (e.g., injection of organics, gases)? Should perform cost analysis to compare pump and treat cost vs. ISRM and polysulfate injection (or organics injection).

Implementation Strategy:
Is the sequence and timing of activities appropriate?
Yes.

Can the technology be implemented cost-effectively?
Maybe. Technology is better suited for source zone, and perhaps use as infiltration application in the vicinity of the source zone to target both the chromium source in the vadose zone and the chromium-contaminated groundwater.

Is the budget and level of effort appropriate for the proposed work?
Yes, although details of the wells, operating costs, etc. are not well described (actually deficient description in this case). Further, this effort/amount should also be justified relative to other available technologies.

Proposed Performance Metrics:
Does the proposed project or activity represent a significant improvement compared to the baseline?
Yes, as there is no current method being employed to tackle the chromium plume in depth. Having said this, the alternative methodologies mentioned above should be considered.

Does the project improve the protection of the Columbia River now or in the future?
Yes, as a temporary barrier, and as an additional element in the line of treatment of the chromium plume.

Are there measurable parameters that would document performance?
Yes. The downgradient groundwater will be monitored for redox-sensitive parameters including dissolved oxygen, oxidation-reduction potential, iron, manganese, lead, and arsenic. However, this statement does not specifically specify concentrations that will indicate success. Chromium concentrations less than 20 ppb is considered success, but what about sulfide migrating downstream that could affect the zero-valent iron ISRM barrier amendment?

Are these included in the proposal?
Yes.

Summary Evaluation:
Strengths oriented towards employment of a test-bed for use of calcium polysulfide micron-sized zero-valent iron solution to enhance mobilization and coverage in zones of primary interest – high permeability areas, including the coupling of laboratory studies, pilot studies in the field, and coring at the completion of the study. Concerns (i) is the correct conceptual model being employed? (i.e., should we not be targeting the source zone?; else this may be an awfully aggressive approach for a broad-based application); (ii) method of identification of injection/withdrawal and influence of heterogeneity (can we really cover the entire plume with the use of three wells?); (iii) costs associated with large-scale, broad-based employment; and (iv) risk associated with potential for calcium polysulfate solution to move downgradient and interfere with ISRM and zero-valent iron amendment.

Reviewer #7

Target Plume/Area: Cr / 100 Areas

Proposal Title: Insitu calcium polysulfide treatment upgradient of the ISRM barrier

Technical Basis of the Proposal:
General

-- This project is generally consistent with previous peer reviews and recommendations. It fits in to a systematic "blended" approach to the challenge of Cr near the Columbia River. The approach also aligns with the NAS/NRC recommendation to DOE that they consider environmental management systems that provide "defense in depth." The dithionite would work synergistically with the ISRM barrier. Since the systems are redundant and partially duplicative, DOE needs to consider that redundancy and assess the value of the action. More information on the systems approach calculations and a more quantitative justification for the synergism and redundancy should be provided by the proposers. The proposal provides a good descriptive justification (aggressive treatment of a high concentration area and increasing ISRM barrier lifetime) but a bit more justification would be useful for an effort of this magnitude.

The project will deploy an insitu technology that has already been field tested at Hanford. It would provide a rapid and measurable impact and would be a clear step toward meeting the Congressional mandate for this supplemental funded program to improve protection of the Columbia River.

<u>Needs more analysis of alternatives and justification of the need for such an aggressive reagent</u> – there are many example reagents that might have similar benefits without some of the risks. Notably, these include widely used and studied biological substrates (e.g., carbon donors) such as lactate, vegetable oil, HRC advanced (an emulsified "oil" with a polylactate chain replacing one fatty acid chain), carbohydrates (e.g., molasses or corn syrup), whey, and many others. These may provide good performance and may last longer. Essentially, all of the options should be evaluated and the "profile" of short term effectiveness and the effectiveness over time should be considered. As with Uranium, the ongoing Hanford HRC studies funded by EMSP should be mentioned and any lessons learned or opportunities brought forward.

As with zero valent iron, the key reactions utilize hydrogen ions and/or generate hydroxide (increasing pH). The hydrogen balance, as well as the electron balance, are key to design and success. More calculations need to be made and contingencies are needed for maintaining control of all of the master variables.

The project considered ecological and environmental impacts from DO reduction associated with the zero valent iron but did not discuss other important zero valent iron chemical impacts such as the potential for high pH (circa 10 to 14). These impacts could include direct impacts or undesirable geochemical effects such as mobilizing and other metals as alkaline complexes.

The injection will tend to target/follow the high permeability zones – What is the impact of this heterogeneity on the expected effectiveness?

Consider application in a different geometry to maximize impact on high concentration plume (e.g., parallel with flow rather than perpendicular.

Cost appears reasonable.

Implementation Strategy:
Schedule is generally reasonable.

Dipole deployment (combination of injection and extraction) may be reasonable.

Proposed Performance Metrics:
Good performance metrics. Particularly good attention to the potential for adverse collateral impacts on water chemistry downgradient. Need to consider pH impacts as well.

Summary Evaluation:
Good proposal but needs more analysis of alternatives and justification of the need for such an aggressive reagent.

Reviewer #8

Target Plume/Area: Hanford, 100-D Area

Proposal Title: *Initial Calcium Polysulfide Test for Accelerating Clean Up of the Southwestern Chromium Plume in the 100-D Area*

Technical Basis of the Proposal:

Is the project or activity based on appropriate and valid science? Yes. This technology has been shown to be effective at removing Cr(VI) at other sites, at full-scale.

What is the technical likelihood of the stated-desired outcome? High, if implemented appropriately.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? The project fits well with the other proposed activities at the site by reducing the flux of chromium and other oxidants to the ISRM barrier thus helping to maintain barrier longevity and removing chemical mass of chromium upgradient.

Is the proposed approach reasonable and practicable? From a chemical standpoint, the approach of using CPS technology is reasonable. There is however, little information provided in the proposal that explains how the calcium polysulfide will be delivered during these preliminary tests or over the long term.

What are the risks or key uncertainties in the proposed action(s)? The key risk is the emplacement of a large mass of elemental sulfur in the aquifer sediments adjacent to the Columbia River. Based on the oxidizing equivalents in the ground water, treating 1.9 million cubic meters of ground water would require the deposition of almost 1,000 tons of sulfur. In agriculture, sulfur is often added to alkaline soils to decrease the soil pH. Sulfur is oxidized by soil bacteria, thereby forming sulfuric acid which is the substance that lowers soil pH. Each 10 pounds of elemental S generates enough acidity to neutralize 30 pounds of lime. Given the potential of the ISRM barrier to raise pH, this acidification may be beneficial overall, but the potential long-term affects of adding large amounts of sulfur to the aquifer should be carefully considered.

Are there clear examples of alternative ideas or proposals that should be considered? Other options are to evaluate the use of an organic amendment alone without CPS or CPS plus an organic nutrient. These options could eliminate or reduce the potential impact of precipitating a large mass of sulfur within the aquifer and may provide additional cost benefits. In addition, the use of CPS as a technology to treat suspected source zones should also be considered (see discussion below).

Implementation Strategy:

Is the sequence and timing of activities appropriate? Yes.

Can the technology be implemented cost-effectively? This technology could provide a significant cost saving when compared to pump & treat.

Is the budget and level of effort appropriate for the proposed work? Budgetary analysis is better addressed by those familiar with costs typically associate with this type of work at national labs.

Proposed Performance Metrics:
Does the proposed project or activity represent a significant improvement compared to the baseline? Yes. The technology offers the potential, depending on method of deployment, to treat the source thereby reducing overall lifecycle costs. In addition, if successfully implemented, the technology could greatly extend the life of the ISRM barrier by removing oxidizing potential of the upgradient ground water.

Does the project improve the protection of the Columbia River now or in the future? Yes. If implemented successfully it could significantly reduce the levels of Cr(VI) reaching the river. Monitoring will need to continue to ensure that changes in DO, pH and other constituents do not adversely impact the river.

Are there measurable parameters that would document performance? Not clearly stated in proposal but it is assumed that these would be similar to those previously used for evaluating the effectiveness of the dithionite barrier system.

Are these included in the proposal? (see above)

Summary Evaluation:
The objective of this proposal is to evaluate an alternative technology, the injection of calcium polysulfide, to enhance the longevity of the current ISRM barrier. If effectively implemented the technology could reduce the lifecycle costs of the ISRM barrier and the pump & treat systems now in place.

However, the addition of possibly large quantities of sulfur to the aquifer should be carefully evaluated along with the short-term effectiveness of the proposed tests. In addition, given the limited reducing capacity of the calcium polysulfide lixiviate, other amendments that are potentially more cost-effective should be evaluated. In addition, the concept of using calcium polysulfide as a remedial option at this site was first introduced as a remedial option that could treat the source area. Because material costs are relatively low, it was suggested that CPS could be infiltrated into suspected source areas without the need for rigorous source area delineation. It was also initially recommended that the CPS be used in conjunction with an organic amendment to provide additional reducing capacity. It is unclear how this treatment will perform as a barrier, but it is likely given the limited reducing capacity of CPS that it will perform significantly worse than the currently emplaced ISRM barrier. Further consideration should be given to the evaluation of other alternatives discussed above.

APPENDIX G

Hanford 100-D Area Treatability Demonstration: Accelerated Bioremediation through Polylactate Injection Field Test

Target Plume/Area: Chromium/Hanford 100D Area

Proposal Title: Hanford 100-D Area Treatability Demonstration: Accelerated Bioremediation through Polylactate Injection

Reviewers: Brian Looney (lead), Todd Anderson, Dawn Kaback and Gene LeBoeuf

Summary

The review panel felt that this was a significantly improved proposal compared to the earlier proposed calcium polysulfide treatment. DOE should consider funding with the following caveats considered and addressed in developing the final work plan:

- Perform a more complete evaluation of alternatives and adjust the proposal as needed (e.g., justify the selected electron donor and well configuration).
- Reduce the Lab and theoretical components of the work and target a total cost of approximately $1000K. The reviewers felt that the initial effort should be a proof-of-principle test, quickly applied in the field, to determine if a low-cost nutrient delivery system can maintain reducing conditions over reasonable time periods to enable a full-scale deployment.
- Develop technically based performance criteria that focus the objective of this effort and cost effectively monitor the action in combination with the other chromium response actions that are occurring upgradient and downgradient.

The proposed approach is an appropriate part of a "defense in depth" concept for immobilizing chromium in the subsurface before it reaches the Columbia River. The proposed action is upgradient of the "to be repaired" ISRM barrier and downgradient of the suspected source areas (for which various ideas for locating and removing/treating are also proposed). The proposed project will produce reducing conditions and reduce dissolved oxygen, nitrate and Cr(VI) levels in the groundwater, thus extending the service life of the ISRM.

Technical Basis:
The project is generally based on established and appropriate science – specifically the use of lactate (in the form of polylactate) to release organic substrates (e.g., organic acids) to the groundwater. These act as electron donors with the primary objective of providing an appropriate biogeochemical environment for removal of electron acceptors from the system (thus increasing the longevity and reliability of the downgradient in situ redox barrier) and a secondary objective of Cr(VI) reduction to Cr(IV). This "systems" approach to addressing the plume is desirable and has the potential to provide an "optimum" solution – low costs for DOE, environmental protection, and minimized risks of collateral environmental impacts. Moreover, the proposal represents a proactive and appropriate response to the specific recommendations provided by the DOE technical peer review panel on the earlier calcium polysulfide treatment proposal. That peer review panel recommended consideration of a less aggressive yet longer lived electron donor to minimize potential collateral impacts and costs, and to maximize effectiveness in terms of key performance parameters such as lifetime of the action.

The project, as formulated, is somewhat inefficient, takes unnecessary technical risk, and lacks clear focus on the objective of the Columbia River supplemental funding:

- While the presentation of the overall strategy and the "defense in depth" concept was good, there was insufficient work done in evaluating and comparing alternatives for this site (i.e., selecting the appropriate electron donor (Reviewers 1, 2, & 4), and in documenting that alternatives such as pump and treat are non-competitive (Reviewer 3)). Cost, longevity, deployability and other factors were insufficiently considered in this proposal. There was concern that polylactate may not meet the requirement for cost effectiveness and may present delivery challenges that would be difficult to overcome (Reviewer 2).
- About half of the effort focuses on theoretical aspects of the migration of field-generated polylactate emulsions through porous media and then developing computer-based models of that process. This proposed work does not properly acknowledge or utilize the available literature on these topics and the proposed implementation does not appear as robust as commercially available emulsified electron donor products (Reviewers 2 and 4). This is not a basic research fund, it was implemented by Congress to provide supplemental funding, where needed, to improve the protection of the Columbia River in cases where the existing systems were not performing adequately.
- Much of the design focuses on lab scale tests and modeling – this type of approach has had limited success in predicting and understanding system behaviors in complex heterogeneous subsurface settings such as the 100D Area of Hanford. This becomes important because there appears to be a bias in the proposal toward using minimal access and then lab testing / modeling (approx $900K) to prove that the system should work. The alternative, a field based paradigm with more robust access using a larger number of wells, has the potential to provide more reliable treatment at a lower cost (All Reviewers).
- The proposed deployment method is not consistent with general practice and should be justified if used (Reviewer 4)

- More of the effort should be applied to monitoring field performance and to monitoring to assure that there are no substantive adverse impacts of the technology on the hydrology, the downgradient wall, or the Columbia River (Reviewer 4).

Implementation Strategy:
The general feasibility of the process was demonstrated in an Office of Science EMSP project at the Hanford 100H Area in the Hanford formation. The project fits in well with the overall strategy for the 100-D Area chromium plume by providing an up-gradient treatment system to supplement the ISRM Barrier. Unfortunately, the proposal as currently structured is not reasonable and not practicable. Key issues are related to implementation and cost effectiveness as summarized below:

- While limited bench tests and modeling may be appropriate, these should not be the focus of the effort. A pilot field test is recommended as the primary method to ensure that heterogeneous fine-grained sediments from the Ringold formation will respond appropriately in terms of geochemistry, longevity, etc.
- A variety of electron donors are commercially available. As a starting resource, vendors' design guidance and recommendations should be used (Reviewer 1, 2 & 4)
- Costs are too high. Much of the detailed lab and theoretical evaluation of multiphase flow (notably, parts of task 3 including subtasks 3.1 to 3.5, and parts of task 2) may not contribute to the objective mandated by Congress for this funding. Specific suggestions on task and scope are provided by Reviewers 2 & 4.
- While the proposal is generally well written, a diagram and scoping level description of the proposed implementation (maps with scales, a cross section, approximate number of wells, approximate amount of electron donor, etc.) should be included to aid in the review. The proposal contained few details on how the proposed project will be carried out in the field. How many wells will be used? Extraction wells? Monitoring wells? The information provided suggests only two wells will be used across the Cr(VI) contaminant plume. The reviewers were skeptical that this would result in a successful implementation even if such a marginal design could be justified by optimistic modeling based on small scale lab studies. (All Reviewers)

Proposed Performance Metrics:
If the project were successful, it could improve the protection of the Columbia River by supplementing the ISRM Barrier. Targeted geophysical monitoring (to track changes and the presence of reduced conditions in the subsurface) accompanied by a groundwater monitoring strategy is a sound monitoring strategy. Please consider the following:

For the 100D systems approach, a focus on chromium reduction may not be appropriate as the oxygen and nitrate are responsible for the bulk of the oxidative potential of the groundwater, impacting the performance of the ISRM Barrier. Thus, performance metrics should be related to specific removal targets for electron acceptor (e.g., oxygen and nitrate) and treatment zone lifetime – these should be determined based on the necessary upgradient protection to ensure the performance of the ISRM barrier. The effective treatment zone may be better defined by geochemical footprints (and possible geophysics (e.g., SP) rather than trying to detect relatively low saturations of bulk electron donor in the subsurface. This is partially captured in the current proposal but needs to be clarified and emphasized.

Reviewer #1

Target Plume/Area: **Chromium/Hanford 100D Area**

Proposal Title: **Hanford 100-D Area Treatability Demonstration: Accelerated Bioremediation through Polylactate Injection**

Technical Basis of the Proposal:

Is the project or activity based on appropriate and valid science?
Yes. The project is based on the polylactate technology developed by Regenesis for the in situ stimulation of microbial communities and reduction of contaminant metals. A field test of polylactate injection has been conducted at the Hanford 100-H area for immobilizing Cr(VI) in the subsurface at this site. This project has successfully reduced and maintained the concentration of soluble Cr(VI) in the groundwater at low levels over the last 1.5 years of operation.

What is the technical likelihood of the stated-desired outcome?
It is likely that if polylactate can be injected into the proper intervals in the subsurface at the Hanford 100-D area the local microbial community will be stimulated and Cr(VI) levels in the groundwater will decrease. Polylactate is a fermentable substrate and produces both hydrogen and lower molecular weight organic acids that are readily oxidized by a host of the aerobic and anaerobic bacteria common to subsurface environments. Upon the depletion of dissolved oxygen, anaerobic metal and sulfate-reducing microbes will produce the required reductants in the subsurface to reduce Cr(VI) to immobile Cr(III). If sufficient polylactate is delivered to the subsurface it should produce and maintain anaerobic conditions for some time to come. A field test of polylactate injection produced reducing conditions that have been maintained for over 1.5 years at the Hanford 100-H Area providing an in situ, long term test of the technique.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable?
The proposed approach is part of a “defense in depth” concept for immobilizing chromium in the subsurface before it reaches the Columbia River. The proposed project is to be deployed in concert with a refurbished ISRM barrier downgradient near the river bank and upgradient treatment of source areas. The proposed project is aimed at producing reducing conditions immediately upgradient of the ISRM thereby reducing dissolved oxygen, nitrate and Cr(VI) levels in the groundwater thereby extending the service life of the ISRM.

What are the risks or key uncertainties in the proposed action(s)?
Care must be taken in ensuring that the polylactate is injected into the subsurface into areas where it can be most effective. This would include wells that intersect strata in the subsurface that carry Cr(VI) and/or significant amounts of nitrate or other oxidants. Similar to the installation of the

This project is the example of an alternative idea. Initially, calcium polysulfide injection was proposed as a strategy for producing reduced conditions in the subsurface. A panel review concluded this strategy was unnecessary given the fact that a successful biostimulation project with polylactate had already been successfully tested at the Hanford 100-H Area.

Implementation Strategy:

The feasibility of the process has already been demonstrated at the Hanford 100H Area but in Hanford formation sediments. There are a few planned bench scale tests to ensure that sediments from the Ringold formation will respond in the same way as Hanford formation sediments. This is appropriate.

There are few details on how the proposed project will be carried out in the field. How many wells will be used? Extraction wells? Monitoring wells? There is one figure included that suggests only 2 wells will be used across the Cr(VI) contaminant plume. Is this true?

Proposed Performance Metrics:

The baseline project was a calcium polysulfide injection strategy which would also be successful but was viewed as unnecessarily harsh by an EM review panel. Bioreduction was offered as an alternative process that would not result in significant introduction of sulfide (Sulfur) to the subsurface and would not adversely affect the ISRM.

Biostimulation using polylactate injection is a via treatment alternative that has been demonstrated to reduce Cr(VI) concentrations in the Hanford subsurface. However, as with any in situ injection process, placement is the key. The injection will need to be monitored to ensure that the polylactate is injected into areas where it can do the most good. A geophysics monitoring program is mentioned in the proposal that should be able to track the presence of reduced conditions in the subsurface at this site. This is accompanied by a groundwater monitoring strategy. This is a sound monitoring strategy.

Summary Evaluation:

The injection of electron donors into the subsurface to stimulate reducing conditions has been a focus of research within Office of Science research programs for many years. Lactate is one electron donor that has been shown to stimulate the activity of microbial communities to produce reducing conditions and stimulate the reductive immobilization of contaminant metals and radionuclides in a great many laboratory sediment incubation experiments. Also, several field experiments, including one at the Hanford 100-H Area, have also shown that lactate can stimulate the activity of subsurface microorganisms to create conditions suitable for the reductive immobilization of metal contaminants such as chromium. I have few doubts that lactate addition to the subsurface of the Hanford 100-D Area will produce similar conditions and will decrease the levels of Cr(VI) in the groundwater at this site provided the lactate can be delivered to the appropriate locations in the subsurface. I am a little disappointed that the proposed workplan reads more like a proposal for similar work investigated during the Hanford 100-H Area test, albeit in a different formation (Hanford formation). I had anticipated that the success of the Hanford 100-H project would have alleviated some of the need for further laboratory and field testing. However, I do understand the need to evaluate Ringold formation sediments. The section on evaluating multi-phase flow appears unnecessary to this reviewer. Certainly, the manufacturer

(Regenesis) has detailed knowledge of the density and viscosity of the polylactate solutions (and various dilutions) and ample experience in its application to subsurface contamination problems to address some of the concerns of the PIs. Regenesis was an active partner involved in the Hanford 100-H Area experiment. What new formulations are proposed to be tested? Something different than was deployed at 100-H? If so, why, and why develop new formulations now? This seems like "fixing something that is not broken."

Overall, this reviewer is generally supportive of the proposed project and recommends that it go forward.

Reviewer #2

Target Plume/Area: **100-D Area Chromium Plume**

Proposal Title: **Hanford 100-D Area Treatability Demonstration: Accelerated Bioremediation through Polylactate Injection**

Technical Basis of the Proposal:

This proposal reflects an attempt to respond to the review of the calcium polysulfide treatment of the 100-D Area chromium plume up-gradient of the In Situ Redox Manipulation Barrier. The concept of providing an up-gradient treatment system to relieve some of the oxidant load on the ISRM Barrier is based upon appropriate and valid science. The likelihood of the stated-desired outcome is possible, but the likelihood that this approach would be cost-effective and could be deployed full-scale is unlikely.

One serious technical issue relates to performance longevity. First of all, the purpose of the up-gradient treatment system should be to remove oxygen and nitrate, which make up 93.4% of the oxidative capacity of the groundwater. The likelihood that the proposed approach is the most cost-effective is virtually nil. The panel that reviewed the calcium polysulfide proposal made a recommendation to consider the application of a bioremediation treatment system based upon recommendations from an earlier panel, which was convened in 2004 to determine the cause of the breakthrough in the ISRM Barrier and to recommend solutions for mending. The concept proposed at that time was to design and implement a *low-cost* up-gradient treatment system to remove *oxygen and nitrate* from the groundwater, so that the ISRM could be targeted towards treatment of chromium. The current proposal, as written, focuses on chromium treatment and does not address the rapid return to pre-treatment dissolved-oxygen conditions. The proposal states (in several places) that the expected longevity of the HRC treatment would be 12 to 18 months. However, the H-Area HRC injection test results show DO in one well increasing after about three weeks; other plots show DO in the down-gradient monitoring well decreasing from ~9 mg/l to ~6 mg/l, with significant DO present in the groundwater (Hazen, personal communication). This DO would still impact the down-gradient ISRM Barrier. Over a 14-month period, DO in the injection well has increased to ~3 mg/l from a minimum of <1 mg/l.

Thus, it appears that to provide the required performance, HRC reinjection would be required within a period of months, continually. The cost of this type of treatment would be astronomical. HRC costs approximately 50 times more than other carbon sources. While it provides double the electron equivalents, it is still significantly more expensive. HRC also has the advantage of greater longevity, but this still does not make up for the cost differential. In addition, HRC has significant issues related to deliverability, as described in the next paragraph. The selection of HRC as the nutrient additive has not been justified. The earlier review panel recommended that alternative nutrients be evaluated, giving four examples to be considered. If this evaluation has been completed, no information on it was provided in the proposal.

The second major technical issue relates to delivery of the HRC. HRC is delivered as an emulsion that is heated prior to injection to lower its viscosity, allowing it to more freely move into the aquifer. Its areal distribution within the aquifer is limited by its viscosity, which increases rapidly as it contacts the "cold" subsurface. The niche for application of HRC is through injection using CPT, where distance between well points would be approximately 5 feet. Use of direct push to inject the HRC is likely not possible at Hanford. Installation of injection wells on 5-foot centers is not practical for Hanford geologic and hydrologic conditions. Thus, a practical delivery system for HRC for a full-scale deployment at Hanford is not plausible. The 2004 technical assistance team recommended addition of low-cost, liquid carbon sources, possibly through up-gradient infiltration galleries. (Their recommendation for injection of HRC was only if the ISRM Barrier wells themselves were to be mended, and they preferred the use of zero-valent iron for that application). If the proposal is revised, it should address evaluation and demonstration of various organic sources through various delivery mechanisms in the field.

Performance of significant modeling and bench-scale work is not necessary at this time. A small field demonstration of the ability of an inexpensive carbon source to promote reductive conditions in the aquifer is the recommended approach to quickly answer whether it is a viable alternative.

There is little information in the proposal about how the HRC will be delivered and also what portions of the aquifer will be treated. Will there be targeted application in preferential pathways within the aquifer?

The proposal as currently structured is not reasonable and practicable. However, the project fits in well with the overall strategy for the 100-D Area chromium plume by providing an up-gradient treatment system to supplement the ISRM Barrier. The key uncertainty related to this proposal is the cost effectiveness of this approach. Alternatives, including other nutrient media and delivery methods, are described within the body of this review.

Implementation Strategy:

Sequence and timing of activities may be appropriate for a research project, but I recommend that the project be focused on a rapid proof-of-principle demonstration. The schedule of more than two years is too long. The technology as proposed cannot be deployed cost effectively. The issues of HRC longevity and delivery are discussed in the technical section above.

The budget does not appear to be appropriate, and there is not enough detail to evaluate it. For example, Task 3 (>$1.0M) contains modeling, bench-scale and field demonstration. So there is no way, given the current information, to assess its validity. Much of the proposed work would be good scientific background information, but may not be necessary. The 2004 technical assistance team recommended going straight to the field and performing a demonstration that would assess various methods of delivery of an inexpensive carbon source while determining performance to induce and maintain reducing conditions. Subtask 1C could likely be cut, as previous projects funded by EM-20 and its predecessor did not require funding to Fluor Hanford (e.g., carbon tetrachloride source term location). Task 2 should be significantly downsized, as there is a body of literature about application of biological additives to promote anaerobic conditions in the subsurface. Subtask 2.3 could be cut and replaced with Subtask 3.5. Subtasks 3.2, 3.3 and 3.4 could also be cut from this phase of the work. There is no way to assess how much this would reduce the proposed cost for the project.

Proposed Performance Metrics:

There is little information in the proposal about performance metrics and the focus on chromium reduction is not the appropriate target, as the oxygen and nitrate are responsible for the bulk of the oxidative potential of the groundwater, impacting the performance of the ISRM Barrier. The performance metrics should be designed around the ability to reduce oxygen and nitrate levels in the groundwater. If the project were successful, it could improve the protection of the Columbia River by supplementing the ISRM Barrier.

Summary Evaluation:

In summary, the proposal addresses a valid technical need to supplement the In Situ Redox Manipulation Barrier oxidative capacity, through implementation of an up-gradient treatment based upon a reductive bioremediation system. However, the proposal must be rewritten if it is to be considered to funding. It proposes an approach that does not provide a cost-effective solution, based upon two factors, treatment longevity and nutrient delivery. In terms of nutrient delivery, an evaluation of carbon source alternatives must be conducted to assess cost and deliverability issues. If a single carbon source is selected, the proposal must include a justification for the selection. Otherwise, the proposal could include evaluation of several options, which must be low-cost alternatives that could be practically implemented full-scale. The proposal must also address delivery options, as they will likely provide the key to successful implementation.

HRC does not meet the requirement for cost effectiveness and presents delivery challenges that cannot likely be met. The proposal should be a proof-of-principle test, quickly applied in the field, to determine if a low-cost nutrient delivery system can maintain reducing conditions over reasonable time periods to enable a full-scale deployment.

Reviewer #3

Target Plume/Area: 100-D Area

Proposal Title: Hanford 100-D Area Treatability Demonstration: Accelerated Bioremediation through Polylactate Injection

Technical Basis of the Proposal:
Is the project or activity based on appropriate and valid science?
Yes. Use of polylactate (PL) to enhance redox barriers in subsurface environments is relatively well-established. The deployment of PL will serve two major objectives in the overall cleanup strategy of this plume: (i) extend the longevity of the ISRM barrier by creating an upgradient treatment zone to reduce the oxidation rate of the barrier; and (ii) reduce the mass and size of the chromium plume.

What is the technical likelihood of the stated-desired outcome? Good. Applications of this technology to Hanford's 100-H Area have demonstrated that it successfully fixes chromium in the subsurface. Concerns remain, however, regarding targeted injection/extraction sites considering heterogeneity of the subsurface in the 100-D Area, locating the chromium plume, the likelihood of maintaining reducing conditions over extended time periods (although likely improved relative to calcium polysulfide), and last, but certainly not least, the cost associated with a full scale-up application for a broad area.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? This effort represents an integral component of an overall systems-based approach to remediate the chromium plume in the 100-D Area. Specifically, this effort is geared towards immobilization of chromium in the ISRM plume by circulating a biostimulant, polylactate, in the aquifer. This may also create a persistent zone of reduction that may continue to treat chromium under natural groundwater flow conditions. Additional projects include (i) reinforcing an existing insitu redox manipulation (ISRM) barrier placed in the 100-D area in 1999; (ii) deployment of an electrocoagulation treatment system as part of an expanded pump and treat system; (iii) location of the chromium sources in the 100-D Area; and (iv) remediation of waste sites along the Columbia by 2012 through the River Corridor. This suite of proposed activities is oriented towards generating a reduction environment.

Is the proposed approach reasonable and practicable?
Yes, although this reviewer has concern regarding the employment of a biostimulant in the complex subsurface of the 100-D area.

What are the risks or key uncertainties in the proposed action(s)?
Risks/uncertainties include: (i) is the conceptual model for chromium plume in the 100-D area correct?; (ii) site heterogeneity causing difficulty in locating and injecting polylactate solution in correct locations; (iii) longevity of injection (how long will an injection last? (supposedly 12-18 months, but will this be the case for the geochemistry of the 100-D Area?; (iv) difficulty in maintaining/measuring/tracking microbial activity and effectiveness in subsurface; (v) potential

for reduction in hydraulic conductivity in vicinity of injection points due to biofouling; (vi) difficulty in understanding multi-phase flow dynamics in such a heterogeneous environment; and (vii) basis for determining required number of wells derived from improved conceptual model.

Are there clear examples of alternative ideas or proposals that should be considered?
Yes. Use of polylactate likely represents an improvement over use of calcium polysufide as a strong reductant. However, pump and treat has been very successful in the 100-K Area. Further, what about the employment of other reduction techniques in depth (e.g., injection of gases)? Should perform cost analysis to compare pump and treat cost vs. ISRM and polylactate injection (or gas injection).

Implementation Strategy:
Is the sequence and timing of activities appropriate?
Yes.

Can the technology be implemented cost-effectively?
Maybe. Technology may be better suited for source zone.

Is the budget and level of effort appropriate for the proposed work?
Yes, although details of the wells, operating costs, etc. are again not well described. Further, this effort/amount should also be justified relative to other available technologies.

Proposed Performance Metrics:
Does the proposed project or activity represent a significant improvement compared to the baseline?
Yes, as there is no current method being employed to tackle the chromium plume in depth. Having said this, the alternative methodologies mentioned above should be considered.

Does the project improve the protection of the Columbia River now or in the future?
Yes, as a temporary barrier, and as an additional element in the line of treatment of the chromium plume.

Are there measurable parameters that would document performance?
Yes. The downgradient groundwater will be monitored for aqueous cation, anion, and trace metal concentrations before and after polylactate injection. In addition, pre- and post-treatment hydraulic responses will be investigated. However, this statement does not specifically specify concentrations that will indicate success.

Are these included in the proposal?
Yes.

Summary Evaluation: Strengths oriented towards employment of a test-bed for use of polylactate solution to enhance mobilization and coverage in zones of primary interest – high permeability areas, including the coupling of laboratory studies, pilot studies in the field, and coring at the completion of the study. Concerns: (i) is the correct conceptual model being employed? (i.e., should we not be targeting the source zone?; else this may be an awfully "delicate" approach for a broad-based application); (ii) method of identification of injection/withdrawal and influence of heterogeneity (can we really cover the entire plume with the use of three wells?); (iii) costs associated with large-scale, broad-based employment; and (iv) risks associated with microbial community, including ability to thrive in treatment area and potential for biofouling to reduce hydraulic conductivity in treatment zones, potentially leading to increased loading on certain segments of ISRM.

Reviewer #4

Target Plume/Area: **Chromium/Hanford 100D Area**

Proposal Title: **Hanford 100-D Area Treatability Demonstration: Accelerated Bioremediation through Polylactate Injection**

Technical Basis of the Proposal:

General Issues:

The project is generally based on established and appropriate science – specifically the use of lactate (in the form of polylactate) to release organic substrates (e.g., organic acids) to the groundwater. These act as electron donors with the objectives of providing an appropriate biogeochemical environment for Cr(VI) reduction and removal of competing electron acceptors from the system (thus increasing the longevity and reliability of the downgradient in situ redox barrier). This "systems" approach to addressing the plume is desirable and has the potential to provide an "optimum" solution – low costs for DOE, environmental protection, and minimized risks of collateral environmental impacts. Moreover, the proposal represents a proactive and appropriate response to the specific recommendations provided by the DOE technical peer review panel on the earlier calcium polysulfide treatment proposal. That peer review panel recommended consideration of a less aggressive yet longer lived electron donor to minimize potential collateral impacts and costs, and to maximize effectiveness in terms of key performance parameters such as lifetime of the action.

Unfortunately, as formulated, the research is not entirely consistent with the traditional implementation and conceptual model for subsurface polylactate application and about half of the effort focuses on theoretical aspects of the migration of field-generated polylactate emulsions through porous media. There is a substantial body of theoretical and practical literature on the injection and migration of emulsified electron donor. This literature is not referenced nor is it beneficially considered in terms of developing an efficient research plan. This issue will be discussed in more detail below along with specific recommendations. The focus of the proposal is substantially too heavy on fundamental research and thus loses focus on the specific objectives mandated by Congress when it provided the enabling supplemental funding – 1) improve DOE efforts to protect the Columbia River from contaminants migrating from the Hanford Site; and 2) provide new or supplementary technology, where needed, to identify and solve contaminant migration issues.

The proposed approach is an appropriate part of a "defense in depth" concept for immobilizing chromium in the subsurface before it reaches the Columbia River. The proposed action is upgradient of the "to be repaired" ISRM barrier and downgradient of the suspected source areas (for which various ideas for locating and removing/treating are also proposed). The proposed project will produce reducing conditions and reduce dissolved oxygen, nitrate and Cr(VI) levels in the groundwater extending the service life of the ISRM.

Specific Issues:

The proposed research is not consistent with the general conceptual model of HRC deployment and use. The proposed material (the polymerized lactate Hydrogen Release Compound™ (HRC) produced by Regenesis) is described by the manufacturer as:
"a viscous, honey-like material rated at 20,000 centipoise."
Composition: Glycerol Tripolylactate
Non-hazardous, food grade product
Packaged and delivered in 30 lb. PVC buckets
Expected shelf-life of material = 3 years

Field Applications include:
Direct-injection (most common) for source area and permeable reactive barrier applications
Re-circulation wells
Straight HRC application in excavations
Straight HRC application in ex-situ soil mixing
Hydraulic fracturing of tight soil media
Fractured bedrock injection using straddle packers
Direct application into wells via gravity feed

The manufacturers preferred instructions for application of traditional HRC and many example papers are on the manufacturer's website. While the instructions do state that the goals of "this approach" is to increase" the spreading and mixing of HRC into the aquifer," these goals are normally accomplished using direct push and close borehole spacing. In fact, HRC is one of the most widely used and successfully applied electron donors for in situ treatment of chlorinated organics and metals such as chromium (the chromium treatment literature was well referenced in the proposal) – the conceptual model developed in the hundreds of applications and the published case studies is based on closely spaced HRC deployment (recognizing that the material has limited mobility and likely migrates only a small distance from the injection point; in many cases any mobility may result from fracturing the formation). The ultimate performance has been judged by the various polylactate components slowly breaking down and releasing organic acids to provide the desired geochemical benefit. Success and zone of influence are typically measured using the spread of the soluble substrates and bulk geochemical conditions (not the presence of HRC as a separate phase) – See Attachment 1. In a general sense, the proposers build on the earlier Hanford HRC test (100H Area) funded by DOE Office of Science in which injections were performed using wells and in which the HRC was field emulsified to maximize penetration. In this test, however, success was ultimately based on the resulting biogeochemical footprint impact zone as described above and not necessarily on direct emulsion transport. The literature also provides specific references to application in low permeability sediments as well as other environments such as fractured rock. Finally, a commercial- standard process to design and implement this technology, while not foolproof, is available (see manufacturer's website) and could be implemented in a defensible manner using a standard engineering approach with confirmatory lab and field studies. As with other vendors of electron donor products, the manufacturer of HRC, Regenesis, has developed design guidance and spreadsheets that provide such information in an easy to use fashion. In my view, the level of effort and focus on emulsion transport are significantly overemphasized in this proposal. If a widespread deployment of an emulsified electron donor is needed (i.e., technically justified), than alternative products should be considered (examples include emulsified vegetable oils or alternative formulations like HRC Advanced). This is discussed in more detail below.

The emulsion transport portion of the research does not properly build on related research on injection of emulsified electron donors. Over the past 5 to 8 years, several investigators (e.g., Bob Bordon) have studied the transport and distribution of emulsified electron donor under a variety of conditions. This research includes both lab studies and field studies and the development of design guides for the Department of Defense (AFCEE). The resulting scientific literature documents a variety of key findings, including: 1) the surface charge of the emulsion (primary) and the emulsion droplet size (secondary) determine migration characteristics and deposition patterns in porous media, 2) field prepared emulsions sometimes have poor properties for widespread deployment while factory produced emulsions have often proven superior because of better control on droplet surface charge, more uniform and controlled droplet sizes, and lower cost (due to minimizing on-site equipment and labor). Such products have been commercialized and are readily available – the commercial products often contain pH stabilizers, important macronutrients, etc. Similar to HRC, standardized design approaches have been developed and are available in spreadsheet form from the manufacturers (e.g., Solution IES) that provide an approximate idea of quantity, spacing and logistics for use. Notably, this research has primarily been on emulsified vegetable oils, but these substrates have performed well in reducing oxygen and other electron acceptors and represent a technically defensible and potentially low cost alternative to a process that advances a deployment concept and/or new product variant of polylactate. Also, if spread of the actual reagent is determined to be a limiting and important objective, a new product, HRC Advanced, was recently developed to fill that void and provide more mobility and solubility. By focusing on the transport properties of field generated emulsion of HRC as a central research objective, the current research proposal does not strongly advance science and does not focus sharply on the primary goal of improving protection of the Columbia River.

There is a need to monitor and assure that there are minimal adverse collateral impacts – even for this "less aggressive" technology. Earlier peer reviews noted concerns related to the potential adverse impacts of the treated water. In responding to Cr(VI) near the river virtually all of the activities proposed for Hanford involve chemical or biological reduction to the less mobile and less toxic Cr(IV). While this is a reasonable paradigm, additional work may be needed to assure that the "cure" (removing ppb levels of Cr(VI) and replacing it with water potentially containing low levels of oxygen and high levels of iron and manganese) does not have similar or worse impacts on salmon spawning zones compared to the original outcrop. This proposal is better than the calcium polysulfide proposal in that the water chemistry changes in the treatment zone (and ultimately downgradient) will not be as extreme and the water chemistry may be more compatible with the ISRM barrier and the proposed mending by Fe(0).

Implementation Strategy:
The general feasibility of the process was demonstrated in an Office of Science EMSP project at the Hanford 100H Area in the Hanford formation. If a similar HRC deployment is planned, a

limited number of bench scale tests and or a pilot field test might be appropriate to ensure that finer grained sediments from the Ringold formation will respond similarly to the Hanford formation. It appears that the known challenges of Hanford drilling (costs, logistics, heterogeneities, etc.) are an important factor in the design and are the basis for selecting wells rather than direct push lances for injection of the donor. If the proposers believe that such limitations mean that the migration of emulsified droplets is a major conceptual issue for this site, then I recommend a different electron donor be considered – an emulsified donor that has already been tested and which is designed for such application and a donor for which the design guidance and protocols have been developed. In all cases, the vendors design guidance and recommendations should be used as the starting point for this work – this will provide numbers and spacings of wells, injection volumes and rates, total donor added, etc. The focus and investment should clearly remain on the protection of the Columbia River. Much of the detailed lab and theoretical evaluation of multiphase flow (notably, parts of task 3 including subtasks 3.1 to 3.5, and parts of task 2) may not contribute to the objective mandated by Congress for this funding. Tasks 2 and 3 represent about $990K out of $1510K – An implementation strategy that reduces the total costs by about 1/3 (to ($1000K) seems feasible given the recommendations herein. Finally, while the proposal is generally well written, a diagram and scoping level description of the proposed implementation (maps with scales, a cross section, approximate number of wells, approximate amount of electron donor, etc.) should be included to aid in the review. To support this peer review I performed the following scoping analysis. Approximating a treatment zone size (1700 m^3), I ran the design spreadsheet provided by Solutions IES to support potential customers (see Attachment 2). This sheet suggests that a complete treatment might be possible using 100 to 200 drums (approximate material costs of $90K to $180K). A dipole design, as appropriately suggested in the proposal, would be reasonable for this site to avoid spreading contaminants and the total deployment could be accomplished with (about) 4 to 8 wells (plus the necessary monitoring). I recommend using 8 or more wells and closer spacing to provide a more robust implementation that can better meet goals in the heterogeneous target site.

Proposed Performance Metrics:
Performance metrics should be related to specific removal targets for electron acceptor (e.g., oxygen and nitrate) and treatment zone lifetime – these should be determined based on the necessary upgradient protection to ensure the performance of the ISRM barrier. The effective treatment zone may be better defined by geochemical footprints (and possible geophysics (e.g., SP) rather than trying to detect relatively low saturations of electron donor in the subsurface. This is generally captured in the current proposal.

Summary Evaluation:
A significantly improved and meritorious proposal. I recommend funding with several caveats. These caveats should be considered in developing a final work plan: 1) recent literature and manufacturers design protocols should be more prominently used in developing the work scope and task objectives/descriptions, 2) If wells are used for deployment and migration of emulsified droplets of electron donor are important to success, then a developed product with the desired characteristics should be considered (rather than trying to create a product for this application), 3) reduce the lab and theoretical work on multiphase flow, 4) clearly develop technically based performance monitoring criteria that consider the objective of this effort in combination with the other chromium response actions that are occurring upgradient and downgradient.

Reviewer 4
Attachment 1

Fact Sheet on the Distribution of HRC in Sediments

Hydrogen Release Compound HRC®

Distribution of HRC in the Aquifer

General Background

The placement of HRC deposition or injection points is a function of how HRC distributes in the aquifer. Molecular transport in a flow field is well defined in the engineering literature, and these Laws of Mass Transport are applied to the movement of substrate and/or contaminant molecules in an aquifer. Specifically, we would like to apply these laws to the movement of the substrate lactic acid and all its breakdown products, including hydrogen. The Laws of Mass Transport are a compellation and include Darcy's Law (which describes advective flow) and Fick's Law (which describes diffusion). The entire mass transport issue is conveniently presented in a single second order differential equation, generally called the Advection-Dispersion Equation, which ties all of the fundamental processes together, specifically advection, dispersion, diffusion, retardation and consumption.

Anaytical solutions to the Advection-Dispersion Equation (Segol, 1994 – specifically Cleary-Ungs) were used early in the development of HRC to gain a basic theoretical understanding of its potential movement in an aquifer. For further details on the Advection-Dispersion Equation see a basic hydrogeology text such as Applied Hydrogeology by Fetter (1994). A more advanced discussion can be found in Contaminant Hydrogeology (1992), also by Fetter, or Ground Water Models (1990), a collective effort available from the National Research Council.

The use of models was part of a basic "sensitivity analysis" to gauge the relative importance of different parameters (advection, dispersion, diffusion, retardation and consumption) in the HRC distribution process. However, the need for this kind of analysis has now been superceded by actual laboratory and field data sets. As any one familiar with models realizes, the experimental data is worth more than the theoretical projections. While experimental data can be used to calibrate theoretical treatments and make them consistently more accurate, the cost and time that would be involved to gather the key variables at an actual site with enough accuracy is often prohibitive. Also, collecting the data with sufficient accuracy may be a difficult to impossible task.

Under these circumstances, what can we then do to understand the process?

First, as discussed, we have field evidence and this will be presented momentarily. Aside from that there is one theoretical excursion worthy of exploration and that concerns the effects of pure diffusion on the movement of HRC in the aquifer. This is an attractive avenue because it gives a concept of molecular movement independent of hydrogeological and biological conditions. It is a first approximation that grounds us in dealing with the more complex features of an advanced argument.

Theoretical Considerations

As discussed, diffusion is presented as a special case because it is fairly straightforward and manageable and gives an indication of the expected movement in an aquifer under ideal conditions. The important breakdown products of HRC (e.g., lactic acid, pyruvic acid and hydrogen) all extinct logarithmically in accordance with the equation for simple diffusion from a point source. This is the simplest case possible (point source in one dimension). It will be followed with experimentally derived values that will be applied to the more complex case of diffusion from a radial system (areal flux in one dimension). This is representative of a column of HRC dissolving in an enclosed tube perpendicular o to the length.

Returning to the simple case to illustrate a few fundamental concepts we have

$$C(x,t) = Co\,[\,\mathrm{erf\,c}\,(x / 2*(D*t)^{0.5})\,]$$

Where C is the final concentration at distance x in cm. Co is the initial concentration, erf c is the complementary error function, D is the diffusion coefficient in cm^2/sec and t is time in seconds.

A case is presented below for diffusion from a point source and is graphically represented in Figure 1. The initial concentration of lactic acid is fixed at 1,000 ppm, which is a conservative concentration for the zone of solubilized material at the interface of the HRC solids and the aquifer. In the example below, it is very important to also realize that this result is expressed in a "conservative background" with no biological or chemical consumption and no aquifer matrix tortuosity. Actual migration patterns will invariably be less than these theoretical maxima.

Table 1. Lactic Acid Diffusion from a Point Source

		Concentration ppm	Distance rad. in cm	Distance rad. in ft
		1000	0	0
		816	87	3
Temperature in °C	= 25	642	173	6
Time in Hours	= 8729 (1 Yr)	485	260	9
Maximum Distance in cm	= 865	352	346	11
Initial Lactic Acid Concentration	= 1,000	245	433	14
		163	519	17
		103	606	20
		63	692	23
		36	779	26
		20	865	28

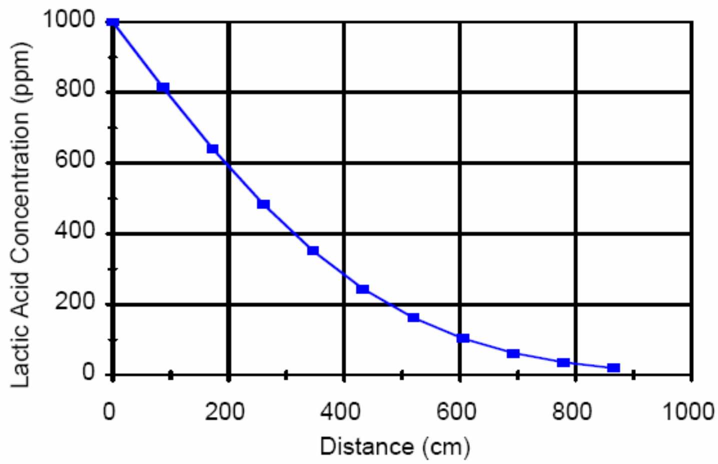


Figure 1. Diffusion of Lactic Acid from a Point Source over 1 Year.

Results show that to achieve a lactic acid concentration of 20 ppm, provisionally enough to treat about 1 ppm of chlorinated hydrocarbon, sources can be as far apart as 56 feet as two 28 foot radii converge between application points. Again, this is in a non-consumptive environment with no path length tortuosity and in a one dimensional diffusion situation. As we will see the more exact result, which is connected to an actual experimental measurement of the diffusion coefficient and involves tortuosity and consumption, values are presented that are about 40 percent of those presented in the above analysis.

The point of this simple exercise is to emphasize that "diffusion matters". Essentially, because the driving force is substantial at 1,000 ppm (versus, say, oxygen at 25 ppm), we can document a fairly vigorous movement of lactic acid and its breakdown products. Diffusion is actually a major driving force in low to moderate flow environments (noting that 0.1 ft/day = 36.5 ft/yr). It is also a valuable force in actually achieving contact between contaminant and substrate, because diffusion is an excellent way to distribute materials in the sub-surface relative to the injection of liquids – an activity that creates preferential flow paths and mixing problems.

Laboratory Results

The next level to examine is laboratory performance. In this instance we performed an ASV test. For further details about the ASV macrocosm test please refer to TB 2.4.3; an illustration of this experimental system is provided in Figure 2.

Figure 2. Aquifer Simulation Vessel (ASV)

The purpose of this ASV study was to accomplish two goals. The first was to determine if the viscosity of the HRC affects the longevity of the product. A high viscosity "implant quality" GPL (approximately 200,000 cP) and the injectable HRC (20,000 cP) were compared. The second goal was to determine the diffusion rate for the two different materials in different compositions of soil. Details on the product viscosity issues and the longevity results are provided in TB 2.8.1.

In establishing the test, a soil sample with an active population of TCE degraders is homogenized by manual stirring and the soil is packed into a series of 6.0-foot long tubes with an internal diameter of 5.75 in. The tube therefore has a volume of 2,025 in^3, and approximately 30% of that volume is pore space. A solution of 25 ppm of TCE was passed through the ASVs to make the concentration of TCE constant throughout. The pumps, which normally are used in the ASV for continuous flow experiments, were turned off and 15 g of HRC was loaded into the front end of each of tube. The ASVs were analyzed monthly until a reasonable diffusion rate was determined, and the experiment was continued to gather HRC longevity data.

Four ASV tubes were set up. Two were packed with 10% loam and 90% clay with 25 ppm of TCE. One of the ASVs was injected with HRC (20,000 cP) and the other with high viscosity GPL (200,000 cP). The other two ASVs were packed with 10% loam and 90% sand with 25 ppm of TCE and each received one of the two different viscosity materials. The flow of TCE solution was stopped once the HRC was injected and the movement of HRC and its by-products was left to diffusion.

The four ASVs were analyzed on day 3 after injection to see if there was any lactic acid present at the six-inch port in order to determine diffusion rates. Lactic acid was present and thus the 12-inch port was analyzed and used to determine the diffusion rates. The results are presented in Table 2.

Table 2. Diffusion in an ASV.

ASV Composition	Rate	GPL-HRC Viscosity
90% Sand-10% Loam	3 in/day	196,000 Cp
90% Clay-10% Loam	4 in/day	196,500 Cp
90% Sand-10% Loam	4 in/day	21,500 Cp
90% Clay-10% Loam	4 in/day	21,500 Cp

The lower viscosity material releases lactic acid at higher rate than the higher viscosity material (Table 3). The major difference between the low viscosity and high viscosity is the amount of lactic acid that diffuses out to a given location with time. As discussed in TB 2.8.1, all other conditions being equal, product viscosity combined with the nature of microbial activity in the aquifer are the ultimate key determinants of product degradation rates. This is essentially a surface area argument. The thinner the material the more it will spread out and be exposed to general chemical and biological degradation. Consequently, the low viscosity material can generate larger concentrations at greater distances from the source, but it will be consumed more readily.

Pyruvic acid is a breakdown product for lactic acid, on the way to acetic acid; a mole of hydrogen is produced at each step. For further details see TB 1.1.3. In Tables 3 through 6, the low viscosity material is already starting to convert to acetic acid, while the higher viscosity product does not have any acetic acid present and is still releasing lactic acid.

The major difference between the low viscosity (20,000 cP) and high viscosity (200,000 cP) products is the amount that diffuses out to a given location with time. This is exactly what is expected. Because bacteria metabolize the low viscosity material more quickly, the concentrations seen at various distances are larger. Of course, the "source" concentration will be used up sooner so that the higher concentrations of lactic acid are offset by the time the lactic acid will be present.

In both cases substantial concentrations of lactic acid (10 – 90 ppm) are seen 1 ft from the source in three days. By day 6, significant concentrations of lactic acid (14-132 ppm) were seen at 2 ft from the source. The concentrations of the low viscosity material are much higher, as would be expected.

Table 3. Organic Acid Data for ASV #1-90% Sand-10% Loam-High Viscosity

	Lactic Acid Results (mg/L)				Pyruvic Acid Results (mg/L)				Acetic Acid Results (mg/L)			
Days	**3**	**6**	**36**	**66**	**3**	**6**	**36**	**66**	**3**	**6**	**36**	**66**
1.0 ft	10.6				0				0			
1.5 ft		2.12				0				0		
2.0 ft			2.74	1.68			0.13	0.07			0	0
2.5 ft												

Table 4. Organic Acid Data for ASV #4-90% Clay-10% Loam-High Viscosity

	Lactic Acid Results (mg/L)				Pyruvic Acid Results (mg/L)				Acetic Acid Results (mg/L)			
Days	**3**	**6**	**36**	**66**	**3**	**6**	**36**	**66**	**3**	**6**	**36**	**66**
1.0 ft	13.3				0				0			
1.5 ft												
2.0 ft		14.2	8.79	23.2		0	0.07	0		0	0	0
2.5 ft												

Table 5. Organic Acid Data for ASV #2-90% Sand-10% Loam-Low Viscosity

	Lactic Acid Results (mg/L)				Pyruvic Acid Results (mg/L)				Acetic Acid Results (mg/L)			
Days	**3**	**6**	**36**	**66**	**3**	**6**	**36**	**66**	**3**	**6**	**36**	**66**
1.0 ft	12.3				0				0			
1.5 ft												
2.0 ft		59.9	1.64	1.26		0	0.09	0.07		0	0	46.4
2.5 ft												

Table 6. Organic Acid Data for ASV #3-90% Clay-10% Loam-Low Viscosity HRC

	Lactic Acid Results (mg/L)				Pyruvic Acid Results (mg/L)				Acetic Acid Results (mg/L)			
Days	**3**	**6**	**36**	**66**	**3**	**6**	**36**	**66**	**3**	**6**	**36**	**66**
1.0 ft	93.1				0				0			
1.5 ft												
2.0 ft		132	138	445		0	0	0		0	27.2	1498
2.5 ft												

In contrast to the previous treatment of diffusion we have here an actual experimental result. Since the diffusion is for a cylinder of HRC rather than a point source we refer to a different equation (Segol, 1994). The basis is:

$$0.02 = \frac{Dt}{r^2} \qquad [1]$$

Where D is the diffusion coefficient in cm^2/sec, t is time in seconds and r is the radius of diffusion in cm.
This is for a cylinder where we want the average concentration to be 2% of the source, e.g. 20 ppm if the source is 1,000 ppm. Fitting the data and converting to the English System, using an average value from the experiments of 1 foot in 3 days, gives an effective diffusion coefficient of 0.007 ft^2/day or (7×10^{-5} cm^2/s) and thus a fairly straightforward and usable diffusion rule is derived:

$$t = 3\,x^2 \qquad [2]$$

Where t is the time in days it takes the front to move out a distance x in feet. Thus, it takes about 300 days to move 10 feet or about 11 feet per year. If a higher concentration is used at the source, the time will decrease. We cannot really project exact amounts at various distances from the data because it is difficult to gauge bacterial utilization rates and localized substrate concentrations. What we do get is a sense of diffusional movement as a function of time at a level quite adequate for project design purposes.

Other observations from the data are as follows. Recall that the soil was infused with a solution of 25 ppm of TCE. For the low viscosity HRC, for example, about 3 times more acetic acid than lactic appears at 2.0 ft on day 66 compared to a ratio of 1 acetic acid to 5 of lactic acid on day 36. There is very little acetic acid seen with the high viscosity material. This indicates a larger potential “waste” factor for very low viscosity materials, such that more hydrogen is produced per unit time than can be used for reductive dechlorination. This would lead to off-gassing of hydrogen and/or the production of excess methane with implications for using liquid substrates like lactic acid or molasses.

Ultimately the point of all this is to determine injection point spacing. A highly detailed answer depends on the bacterial activity and product viscosity, but nominally it appears that diffusion alone will drive the lactic acid out several feet in two months. The data suggest that 10 ft points will work if coverage is desired in two to three months. The distance between 10 ft points where coverage occurs is where the two fronts meet at a 5 ft distance from both injection points. Placing 5 for x in equation [2] results in a time of 75 days. If injection wells were placed 20 feet apart they would meet at a distance of 10 feet from each point. This would occur in 300 days according to equation [2]. In a year the distance increases to 11 feet. Note that this assumes no advection whatsoever. The motive force is simply diffusion.

Field Results

The data in Table 7 provide an excellent cross section of results across 10 sites. These are the same 10 sites referenced in the longevity Technical Bulletin (TB 2.8.1). The sites have a range of groundwater velocities from essentially static (Site 1) to moderate flow rates of about 128 ft/yr. (Site 5). All of these sites were treated with 20,000 cP HRC injections, noting that an "injection" is not a process that sends material as far from the injection point as might happen with thin liquids. Therefore, the movement as measured is due to the net mass transport forces of advection, dispersion, diffusion, retardation and consumption. Overall it seems that HRC applied to an aquifer can move quite readily.

Table 7. Movement of Organic Acids in the Field.

ID	Distances and Days to Wells	GW Velocity (ft/yr)	Potential Yearly Movement (ft)
Site 1	8' in 89 days (OW-201-S)	0.15	33
Site 2	20' in 32 days (MW-8, 23 and 27)	110	228
Site 3	16' in 35 days (MW-31)	110	167
Site 4	15' in 154 days (MW-3)	27.4	36
Site 5	32' in 31 days (IMPM-6)	128	377
Site 6	NA*	14.6	NA
Site 7	5' in 33 days (TWM-B)	< 36.5	55
Site 8	20' in 30 days (MW-26)	102	243
Site 9	140' in 140 days (MW-9)	< 36.5	365
Site 10	25' in 120 days (RW-68)	73	76

* NA (not applicable): acids data, which was supposed to be collected at 30 days was not collected until 77 days post-application. At this time acids were detected in monitoring wells, but they were all within a few feet from the HRC grid area. There were no monitoring points downgradient from the grid that were useful in this analysis.

One of the most interesting observations from this data set is the fact that Site 1 is essentially driven by diffusion and is also affected by retardation and, more importantly, consumption. Therefore, we note that there is at least 33 ft of movement per year under these conditions. Recognize that the thesis throughout the entire presentation is the justification for placing 20,000 cP material at 10 ft centers and 200,000 cP material at 20 ft centers.

References

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Fetter, C.W. 1994. Applied Hydrogeology. Macmillan College Publishing Company, New York.

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HRC Technical Bulletin 2.4.3. Aquifer Simulation Vessel (ASV) Studies.

HRC Technical Bulletin 2.8.1. HRC Performance Characteristics- Longevity.

National Research Council. 1990. Ground Water Models- Scientific and Regulatory Applications. National Academy Press, Washington D.C.

Regenesis Web Site. http://www.regenesis.com.

Segol, G. 1994. Groundwater Simulations. Prentice Hall, New York

Reviewer 4
Attachment 2

Emulsified Vegatable Oil (EOS™) Scoping Calculation

EOS
EOS Remediation, Inc.

Emulsified Edible Oil Design Software
for EOS® Family of Bioremediation Products

Version 2.02 Rev. Date: June 16, 2006
www.EOSRemediation.com

Help

Site Name:	Scoping Calculation
Location:	Hanford 100 Area
Project No.:	DOE Peer Review

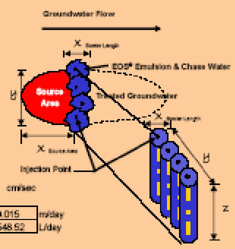
Step 1: Select a Substrate from the EOS® Family of Bioremediation Products

Substrate Selected (pick from drop down list) EOS 598B42
For Product Literature Click Here

Step 2: EOS® Consumption During Contaminant Biodegradation / Biotransformation

Section A: Treatment Area Dimensions

Length of treatment area parallel to groundwater flow, 'x'	30	ft	9.1	m
Width of treatment area perpendicular to groundwater flow, 'y'	900	ft	274.3	m
Minimum depth to contamination	10	ft	3.0	m
Maximum depth of contamination	30	ft	9.1	m
Treatment thickness, 'z'	20	ft	6.1	m
Treatment zone cross-sectional area = y * z	18,000	ft^2	1,672.3	m^2



Section B: Groundwater Flow Rate / Site Data

Soil Characteristics

Nominal Soil Type (pick from drop down list) Silt

Hydraulic Characteristics

Total Porosity (accept default or enter n)	0.43	(decimal)		
Effective Porosity (accept default or enter n_e)	0.10	(decimal)		
Hydraulic Conductivity (accept default or enter K)	1	ft/day	3.5E-04	cm/sec
Hydraulic Gradient (accept default or enter i)	0.005	ft/ft		
Non-reactive Transport Velocity (V_t) = K * i / n_e	0.05	ft/day	0.015	m/day
Groundwater flow rate through treatment zone (Q)	673.20	gallons/day	2548.52	L/day

Section C: Calculated Contact Length (x) = C_t * V_s

Contact time (Ct) between oil and contaminants (accept default or enter Ct)	60		typical values 60 to 180 days, see comment
Calculated Contact Length (x) = Ct * V_s — Suggested Minimum	5.0	ft	

Treatment zone volume	540,000	ft^3	15,291	m^3
Treatment zone groundwater volume (volume * effective porosity)	403,920	gallons	1,529,110	L

Section D: Design Lifespan For One Application

Design Lifespan For One Application	10	year(s)	typical values 5 to 10 years	
Estimated total groundwater volume treated over design life	2,861,100	gallons	10,831,194	L

Section E: Electron Acceptors

Inputs	Typical Value	GW Conc. (mg/L)	MW (g/mole)	e⁻ equiv./ mole	Stoichmetry Contaminant/H_2 (wt/wt H_2)	Hydrogen Demand (g H_2)
Dissolved Oxygen (DO)	0 to 8	5	32.0	4	7.94	6823.231029
Nitrate Nitrogen (NO_3^- - N)	1 to 10	62	62.0	5	12.30	54579.48772
Sulfate (SO_4^{2-})	10 to 500	50	96.1	8	11.91	45459.22552
Tetrachloroethene (PCE), C_2Cl_4			165.8	8	20.57	
Trichloroethene (TCE), C_2HCl_3			131.4	6	21.73	
cis-1,2-dichloroethene (c-DCE), $C_2H_2Cl_2$			96.9	4	24.05	
Vinyl Chloride (VC), C_2H_3Cl			62.5	2	31.00	
Carbon tetrachloride, CCl_4			153.8	8	19.08	
Chloroform, $CHCl_3$			119.4	6	19.74	
sym-tetrachloroethane, $C_2H_2Cl_4$			167.8	8	20.82	
1,1,1-Trichloroethane (TCA), CH_3CCl_3			133.4	6	22.06	
1,1-Dichloroethane (DCA), CH_3CHCl_2			99.0	4	24.55	
Chloroethane, C_2H_5Cl			64.9	2	32.18	
Perchlorate, ClO_4^-			99.4	8	12.33	
Hexavalent Chromium, Cr(VI)			52.0	3	17.20	
User added						
User added						
User added						

Section F: Additional Hydrogen Demand and Carbon Losses

Generation (Potential Amount Formed)	Typical Value	GW Conc. (mg/L)	MW (g/mole)	e⁻ equiv./ mole	Stoichmetry Contaminant / H_2 (wt/wt H_2)	Hydrogen Demand (g H_2)	DOC Released (moles)
Estimated Amount of Fe2 Formed	10 to 100	50	55.8	1	55.41	9774.160849	
Estimated Amount of Manganese (Mn^{2+}) Formed		5	54.9	2	27.25	1987.10551	
Estimated Amount of CH_4 Formed	5 to 20	10	16.0	8	1.99	54438.8578	
Target Amount of DOC to Release	60 to 100	100	12.0				90177.29

Calculations assume:
1.) all reactions go to completion during passage through emulsified edible oil treated zone; and,
2.) perfect reaction stoichiometry.

EOS® Requirement Calculations Based on Hydrogen Demand and Carbon Losses

Stoichiometric Hydrogen Demand	381	pounds
DOC Released	5,148	pounds

EOS® Requirement Based on Hydrogen Demand and Carbon Loss
21 drums

Step 3: EOS® Requirement Based on Oil Entrapment by Aquifer Materials

Soil Characteristics

Density of Sediment (accept default or enter site specific value)	130	lbs / ft3
Effective Thickness (typically less than 40%)	0.25	
Weight of sediment to be treated	17,550,000	lbs
Adsorptive Capacity of Soil (accept default or enter site specific value)	0.004	lbs EOS® / lbs sediment

For Additional Information on Effective Thickness, Click Here

Oil Retention by Sediment[1]
- Fine sand with some clay 0.001 to 0.002 lbs EOS® / lbs soil
- Sand with higher silt/clay content 0..002 to 0.004 lbs EOS® / lbs soil

[1] Default values provided based on laboratory studies completed by NCSU
For Additional Data, Click Here

EOS® Requirement Based on Oil Entrapment by Aquifer Material
168 drums

Summary – How much EOS® do you need?

Suggested Quantity of EOS® for Your Project: 168 drums

EOS Remediation, Inc.

Help

Emulsified Edible Oil Design Software
for EOS® Family of Bioremediation Products
Version 2.02 Rev. Date: June 16, 2006
www.EOSRemediation.com

Site Name:	Scoping Calculation
Location:	Hanford -- 100 Area
Project No.	DOE Peer Review

Emulsion Makeup

Concentrate : Water Ratio (1 Part EOS® Concentrate to)	10	water	Minimum Value = 4; typical values 4 to 10	
Approximate Quantity of Emulsified edible oil substrate f	70,560	pounds	9240	gallons
Length of treatment area parallel to groundwater flow, "x"	100	ft		
Effective treatment thickness, "z_e"	5	ft	Accecpt calculated or enter site specific value	

Number of Injection Points and Dose:

Spacing between injection points	30	ft on center spacing within rows between injection points (typical values 5 to 15)		
Number of injection rows	1			
Overlap between injections, percent	0%	typical values 25 to 50%		
Number of injection points	4	points		
Emulsified edible oils injected per point	17640	pounds	2310.0	gallons
Injection zone diameter	30	feet		
Pore volume per injection point	2,644	gallons		
Displacement flush pore volumes	1	typical values 0.5 to 1.25		
Displacement flush volume per point	334	gallons		
Total Injection volume per injection point	2,644	gallons		

If the **EOS®** concentrate is diluted in the field with 10 parts water, no additional chase water may be needed. However, the injection of additional chase water may help distribute the emulsion in the aquifer.

APPENDIX H

Field Test Electrocoagulation for Accelerated Clean Up of the Northeastern Chromium Plume in the 100-D Area

Target Plume/Area: Chromium / Hanford 100-D Area

Proposal Title: Field Test Electrocoagulation for Accelerated Clean Up of the Northeastern Chromium Plume in the 100-D Area

Proposal Reviewers: Brian Looney, Todd Anderson, David Cocke, Miles Denham, Dawn Kaback, Gene LeBoeuf, David Lesmes, Bill Malyk.

Summary Evaluation:
The panel generally supports performing the electrocoagulation (EC) field test to determine the ability of EC to optimize the existing pump and treat system to accelerate the reduction of the Cr(VI) contaminant plume in the Hanford 100-D Area. However, the panel identified several specific technical and implementation components of the EC system that need to be carefully addressed, identified, or evaluated. Also, other viable alternative technologies, should be screened to confirm/assure the selection of EC. The panel expressed concern over the requested funding and provided input on strategies to maximize value.

Technical Basis of the Proposal:
The panel believes the proposed project fits well into the systems approach to accelerate the cleanup of Cr(VI) contamination near the Columbia River. The project is based on valid and appropriate science

General technical issues for consideration:

- Electrocoagulation (EC) is a complex system, so designing for versatility is critical. The system should be robust enough to enable rapid adjustments in the field to allow the system to adapt to field conditions and to allow flexibility in operation. (see reviewers 2, 7, and 8)

- EC is scalable to the size of the plume area and is compact. If it is designed correctly, it can be used at one or at multiple sites. Coupled with re-injection, it may provide opportunities for "defense in depth;" (all reviewers)

- Consider recharge in the on site basin and other creative options for the treated water – The available options and ultimate use of the treated water should be a principal factor in the design since EC systems can be operated to yield a wide range of output water chemistries (e.g., targeted pH or eH levels) depending on needs. (see reviewers 2, and 7)

- Vendor selection is of paramount importance; the panel recommends development of clear parameters for consideration during vendor selection. Don't base vendor selection on treatability alone. (all reviewers)

- Because EC appears to be a simple technology, many vendors attempt to build and market systems. Some of these EC systems have been "oversold," which may result in stakeholder confidence issues. (see reviewer 2)

- The panel provided several specific technical recommendations. These are summarized in a special box after the "Performance Metrics" below.

- Perform a complete analysis of groundwater and effluent criteria to determine the end uses of water processed through the EC system. (see reviewers 2, 7, and 8)
  - Consider re-injecting water passing through the EC system upgradient or into the contaminated basin, to integrate with the other proposed Cr(VI) treatment technologies.
  - The chemistry of the water coming out of the EC system, such as the pH and the ionic strength, is very important. If water has to be treated before re-injection, project costs will increase.
  - More information about the flow rates is necessary to design an effective EC system.
  - Address the potential for formation of an impermeable oxide film on the cathode causing a decrease in system efficiency.

- Consider results from an "alternatives analysis" comparing ion exchange technology with EC and other treatment methods to determine the most effective and appropriate technology. (see reviewers 1,2,
  - Consider all applicable and viable alternative technologies.
  - Identify the impacts of increased pumping of groundwater.
  - Consider the production and disposal of solid waste "sludge" material in the various alternatives.
  - Consider the impact of the Hanford groundwater's low conductivity on the function of an EC system.

Implementation Strategy:

- The sequence and timing of project activities are generally appropriate.

- Most vendors have a scoping process for process development and optimization based on site-specific water chemistry and effluent water quality needs. These scoping activities are normally performed for a very low cost. Working with that model, the overall project costs may be able to be reduced significantly (for example, eliminating some of the miscellaneous engineering hours associated with the onsite design). (see reviewer 2)

- Although studies have documented that the historical costs for an EC system are relatively low compared to ion exchange, the total labor hours in those studies was higher for EC than other technologies -- thus, DOE labor rates are an important factor in the design and implementation and the panel recommends a system that can operate with minimal labor. Labor costs need to be optimized in order to make EC cost-effective. (see reviewer 7).

- Provide more detailed description of project management and engineering costs. The cost of this one technology test is currently 20% of the total congressional allocation, which seems very high when viewed as a water treatment cost. (see reviewers 2, 6, 7, and 8)

- The proposed project implementation schedule may be overly optimistic. Equipment procurement usually takes more than 8 weeks. (see reviewers 2, and 8)

- If the Department of Energy provides $2 million to fund an EC project, is appears that scope could be included to optimize the pump and treat system and/or to consider other viable options. (all reviewers)
  - It is important to simultaneously optimize the pump and treat system when designing and locating the EC system, determining where to re-inject or re-infiltrate recycled water, and where to identify the capture zones.
  - Improve the conceptual model for how the EC system would operate.
  - Evaluate alternative beneficial strategies for disposing of or re-injecting water passed through the EC system.
  - Conduct the field test concurrently with efforts to identify infiltration zones, well placement, etc.
  - Determine costs associated with solid waste disposal, power consumption, operation and maintenance, and discharge of treated water.
  - If the alternatives analysis indicates other technologies should be considered, the scoping test should include these additional technologies.

- Try to utilize existing expertise in industry to minimize training costs. On-site training would be beneficial to the workers who would actually operate the system. (see reviewer 2)

Proposed Performance Metrics:

- Develop performance metrics for all aspects of the EC system design, including design specifications, vendor selection, effluent water quality, etc.
- Performance metrics should report increased flow rate and Cr(VI) concentration reduction (<20ppb).
- Demonstrate operational reliability and safety of the EC system equipment.
- Measure pressure and flow data to monitor the operation of the EC system.
- There will be some interaction with soil, so predictions about when the system is finished may have to be extended to allow further time to remove Cr(VI) from solids.

Specific Engineering and Design Recommendations

The electrocoagulation unit(s) should have the following to provide a very versatile system, to cover the anticipated variability of the treatment requirements, and have operation with minimum operator oversight:

1) The capacity to allow uninterrupted collection of water and be continuous at a rate independent of but less than the system's treatment capacity
2) Have the capacity to function between ~250 to 500 gpm and be modular in design (have at least two high flow easy accessible cartridges) to allow uninterrupted changing of electrode plates without stoppage of the unit but possibly with reduced flow
3) The EC system should have built-in versatility of electrode arrangement to accommodate the field flexibility needed to treat the water at the Hanford 100-D Area. The system's electrode arrangement should be made easy to change in the field and have provisions for very rapid change-out of plates by cartridge design and mechanical devices that remove and replace cartridge as a unit and without removing flanges and bolts to the extent possible.
4) Have a de-foam tank that has the capability of adding coagulation polymers or not; which may fit with the integrated plan to add bio-nutrients to the plume for added reducing capacity
5) Have a water clarification system (possibly based on slant-plate technology) for the clarifiers that is low corrosion with the capability of adding coagulation polymers or not; which may fit with the integrated plan to add bio-nutrients to the plume for added reducing capacity
6) Allow treated water to be discharged by gravity or pumping back to injection wells in the drain field.
7) Allow protection of the reducing capacity (avoidance of uncontrolled exposure to air) of the EC treated water to be sent to injection wells (this could use a physical or nitrogen blanket for example)
8) Be adjustable to control the rate of production not to exceed the injection well reception capacity if necessary
9) Allow the solids to be automatically and efficiently collected in a filter press hopper with liquid discharge from the clarifier or similar device
10) Meet National Electrical Code safety requirements in all respects. Ensure vendors use a system that operates below 40 volts; higher voltage systems present safety and electrical code concerns.
11) Be mountable on a prepared concrete or other surface with some protection against spills
12) Have the capability of rapid infield changing of the electrode arrangements from monopolar to bipolar and with variation of anode and cathode surface areas.
13) If DC, have the capability of automatic reversal of electrode polarity to prolong electrode life (avoiding reversal with contacts under load)
14) Will include electrical distribution and automated controls for minimum operator attention.
15) Have electrodes that are simple plates that can be changed without special tools or welding
16) Have provisions that allow the system power supply (rectifier) to be capable of maintaining the selected amperage even if the conductivity of the water changes by a considerable degree to avoid excursions or lack of treatment as various changes occur in the water
17) Have capability to run reliably for a long periods at high duty cycle.

Reviewer #1

Target Plume/Area: Chromium/Hanford 100-D Area

Proposal Title: Field Test Electrocoagulation for Accelerated Cleanup of the Northeastern Chromium Plume in the 100-D Area

Technical Basis of the Proposal:

Is the project or activity based on appropriate and valid science?

Electrocoagulation appears to be capable of treating large volumes of pumped groundwater very rapidly and presumably can treat water with high concentrations of the contaminants (i.e chromium).

What is the technical likelihood of the stated-desired outcome?

An expanded groundwater pump and treat system is planned for the Hanford 100-D area. The current treatment system(s) is not capable of handling the increased volume and, in some cases, the increased Cr content expected with the expansion of the system. The EC method has been identified as a method capable of handling the increased volumes and concentrations of Cr. However, it is not clear what the impact on the site will be. A field test is planned to try EC in manner consistent with the planned P&T expansion. I think it is reasonable to expect more Cr(VI) removal but how much more will be determined in the field test.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable?

There is a need for increased volume of groundwater pumping in the 100-D Area. Current ion-exchange techniques are inadequate and must be regenerated offsite or replaced. The proposed electrocoagulation process can treat the expected volumes of groundwater requiring pumping and appears to be able to be maintained/serviced on site. The expanded pump and treat system is an improvement to the existing system but may not exceed the existing in removing contaminants from the site.

What are the risks or key uncertainties in the proposed action(s)?

The risk is that the EC system does not perform as indicated and/or requires much more maintenance/servicing than more conventional techniques. An overall risk at the site is that the expanded pump and treat system fares no better at removing contaminants from the subsurface than the original system.

Are there clear examples of alternative ideas or proposals that should be considered? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)

I have no clear alternative suggestions but nevertheless would ask the PIs to at least have a “plan B” written out in the proposal in case EC does not perform as planned. Plan B could simply be an expansion of the current P&T methods.

Implementation Strategy:
(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work?

The proposed field test of the EC method and the timing seem to be appropriate. My sense is that evaluation of the EC method can be performed relatively rapidly. I am OK with the proposed timing of the project.

Since the expanded P&T system is planned for an area separate from the plume containing the ISRM there should be minimal impact of the EC systems on the performance metrics for the ISRM mending and reduction activities. However, a contingency P&T system for the ISRM area using EC, if appropriate, should be a part of the overall "systems treatment" plan for the entire area.

The budget (>$2M) requires more clarity i.e. what tasks does "engineering hours" entail? Please provide additional detail on the items in the budget.

Proposed Performance Metrics:
The EC method should be demonstrated to remove the highest expected Cr concentrations to levels below the 20ppb limit in the highest throughput volumes possible. The field test should not only simply test the EC method but also push the limit of the technology. For a given Cr concentration, how much groundwater can you treat before Cr is not effectively removed to the 20ppb limit?
Other critical factors to demonstrate performance in addition to Cr removal and treatment throughput; 1) power consumption costs, 2) solid waste disposal costs, 3) maintenance costs, 4) discharge method/cost of treated water.

Summary Evaluation:
A planned expansion of the P&T system at the 100-D area requires a more robust water treatment system to handle large volumes of Cr-contaminated water (some areas containing very high levels of Cr). The EC method has been identified as a possible technology capable of meeting the requirements of high throughput and potentially high Cr concentrations. A field test of this method is planned for 100-D area. I have no objections to examining this technology for use at the 100-D area. If the EC works as expected the expanded P&T system is an integral part of the overall "systems" approach to site remediation in this area.

I recommend that this proposal move forward.

Reviewer #2

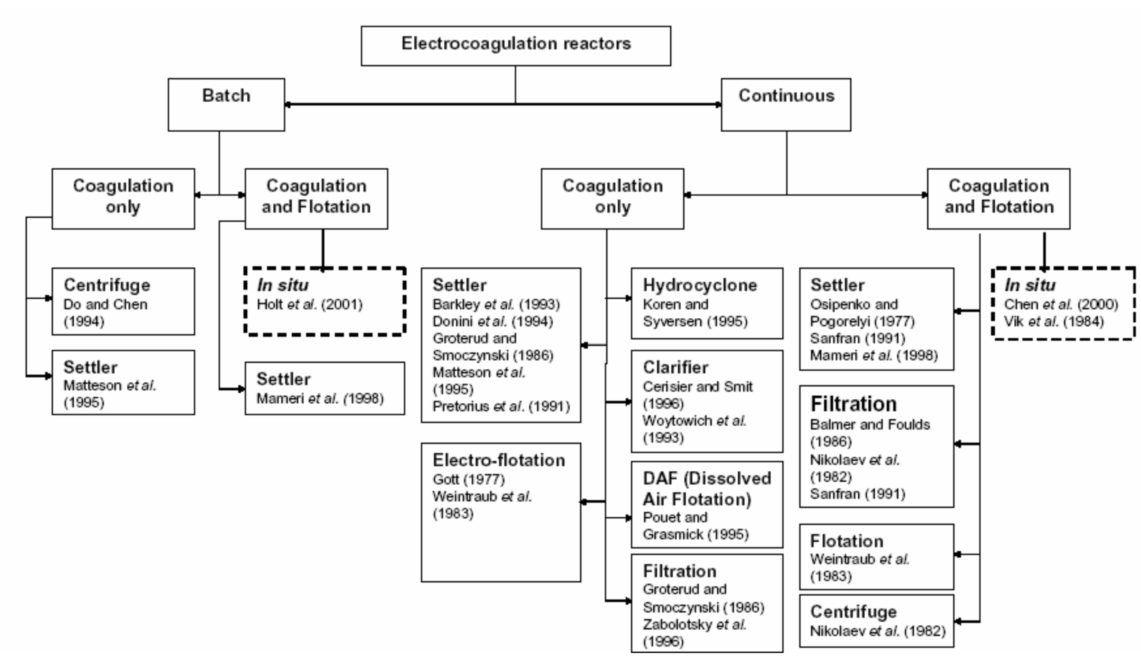
Target Plume/Area: Hanford Site, 100-D Area

Proposal Title: Field Test Electrocoagulation for Accelerated Clean Up of the Northeastern Chromium Plume in the 100-D Area

Technical Basis of the Proposal:

Is the project or activity based on appropriate and valid science? What is the technical likelihood of the stated-desired outcome?

Yes, the project is based on appropriate and valid science. Electrocoagulation (EC) is a process that generally works well with chromium. It involves the reduction of Cr(VI) to Cr (III) in the process and utilizes the reductive capacity of Fe(II) ions injected into solution. The subsequent oxidation of Fe(II) to Fe(III) by Cr(VI) and other species produces solids that by chemical incorporation and adsorption capture Cr for its removal by various techniques summarized by Holt (Chemosphere 59 (2005) 355-367):



The choice is generally dictated by current density requirements. Although the science is both appropriate and valid, the actual implementation of the technology needs to be carefully planned and needs to be based on the appropriate and valid science and not on the "black box approach" that has plagued EC for decades.

Given that a thorough chemical basis is established for the application of the EC technology based on the solution chemistry, electrochemistry and interfacial chemistries and that the other ground water manipulations are carefully taken into consideration, the technical likelihood of the stated-desired outcome is quite high.

How does the project fit in with the totality of proposed activities for the target contaminant/plume?
The application of EC technology fits well with the totality of the proposed activities for the target chromium and the plume(s) identified in the 100 D area. The refinement of the location of the Chromium Source in the 100 Areas is appropriate for the application of the EC technology since it can be directly applied to the localized problem area as a major strength of EC is its mobility and capacity to be distributed to problem areas. The application of Calcium Polysulfide is also quite compatible with EC technology. It is chemically related since the goals of the two technologies are to ultimately chemically reduce the Cr(VI) to Cr(III). However, it is yet to be determined if the additional species introduced into the plume water will interfere with the EC process.

Is the proposed approach reasonable and practicable?
The new, integrated approach to accelerate cleanup of chromium in the 100 Areas is absolutely the most reasonable and practicable approach. The integrated approach of using an insitu reductant, building more robustness in the ISRM's and using a chemically complementary technology of EC is excellent. Again, there is a need to explore the synergistic aspects of the three approaches as well as the interferences such a surface passivation of the zero valent iron by sulfides and sulfates as well as the interferences in the EC process that might result from the insitu processes.

What are the risks or key uncertainties in the proposed action(s)?
In chemical environmental remediation, the complexities of the coupled chemical and physical system have masked possible new problems that can occur. Here the coupled chemical consequences of each action that is being taken needs to be carefully considered. The risks are moderated by the common objective of producing immediate activity and residual capacity to reduce the Cr(VI) to Cr(III). However, the addition of new sulfur related chemistries on solution and interfacial properties need to be delineated.
There does not seem to be any major risk of an accelerated failure of the ISRM or the pump and treat plans using EC.

Are there clear examples of alternative ideas or proposals that should be considered?

In the particular case of electrocoagulation, the electrochemical injection on Fe(II) into the solution using Fe Anodes and the possibility of re-injecting the EC treated (i.e. Fe (II) amended) water, which can have substantial reductive capacity, back into the plume, particularly at strategic locations, (Plume front, Plume edges, etc.) needs to be considered.

Implementation Strategy:

Is the sequence and timing of activities appropriate?
Yes, the sequence is appropriate to the scale and scope or the project.

The summary implementation schedule provided in Figure 3 assumes that the authorization to proceed is given prior to April 1, 2006 and that any HQ peer review is also completed before April 1, 2006.

Can the technology be implemented cost-effectively?
Yes, the cost of EC continues to be competitive with the most cost effective chromium treatment technology available.

Is the budget and level of effort appropriate for the proposed work?
Yes.

Proposed Performance Metrics:

Does the proposed project or activity represent a significant improvement compared to the baseline?
With the objective of the new approach to significantly shrink the chromium plumes while continuing to protect the ecological receptors and human health at the river, the proposal represents a significant improvement compared to what is being done and what has been done. Considering the baseline being the existing ion exchange technology to treat the extracted water and then re-injecting the treated water into the aquifer in the northeastern portion of the 100-D chromium plume, the proposed EC technology is a significant improvement.

Increasing the pace of groundwater remediation by deploying an electrocoagulation treatment (EC) system(s), which is/are capable of treating high flow rates and high concentrations of chromium is a very significant move in the right direction since the existing ion exchange technology cannot support the more aggressive treatment scheme proposed.

Does the project improve the protection of the Columbia River now or in the future?
Yes, significantly when implemented but it has the longevity to have the desired impact in the future. If EC treatability tests determine the process to be a viable technology for treating the chromium plume, its application to aggressively cleanup the northeastern chromium plume at 100-D would dramatically improve the protection of the Columbia River. The plan to have a 500 gpm EC unit if the technology is successful needs to be carefully considered against several EC units statically located to provide maximum impact. Either approach would significantly accelerate cleanup since the two existing pump and treat systems, treat only a total of 140 gpm.

Are there measurable parameters that would document performance?
Demonstration of EC capability to reliably reduce Cr(VI) to <20 ppb prior to re-injection
Characterization of the EC byproducts (minimize Magnetite) for waste disposal
Determination of the efficiency of the Cr(VI) removed (Cost of equipment , materials, utilities, chemicals, waste handling, management and M&O)
Demonstrated operational reliability and safety of the equipment
Measured operational data to support the EC system (Pressure and flow)

Are these included in the proposal?
Yes

Summary Evaluation:
The proposal work would be a major step forward in the protection of the Columbia River and is recommended to move forward with adequate considerations given the points made in the review. The EC technology chosen must be based on science directed EC process engineering and must be versatile enough to adapt to the requirements.

The electrocoagulation unit(s) should have the following to provide a very versatile system, to cover the anticipated variability of the treatment requirements, and have operation with minimum operator oversight:

1) The capacity to allow uninterrupted collection of water and be continuous at a rate independent of but less than the system's treatment capacity

2) Have the capacity to function between ~250 to 500 gpm and be modular in design (have at least two high flow easy accessible cartridges) to allow uninterrupted changing of electrode plates without stoppage of the unit but possibly with reduced flow

3) Have provisions for very easy and rapid changing of plates by cartridge design and mechanical devices that remove and replace cartridge as a unit

4) Have a de-foam tank that has the capability of adding coagulation polymers or not; which may fit with the integrated plan to add bio-nutrients to the plume for added reducing capacity

5) Have a water clarification system (possibly based on slant-plate technology) for the clarifiers that is low corrosion with the capability of adding coagulation polymers or not; which may fit with the integrated plan to add bio-nutrients to the plume for added reducing capacity

6) Allow treated water to be discharged by gravity or pumping back to injection wells in the drain field.

7) Allow protection of the reducing capacity (avoidance of uncontrolled exposure to air) of the EC treated water to be sent to injection wells (this could use a nitrogen blanket for example)

8) Be adjustable to control the rate of production not to exceed the injection well reception capacity if necessary

9) Allow the solids to be automatically and efficiently collected in a filter press hopper with liquid discharge from the clarifier or similar device

10) Meet National Electrical Code safety requirements in all respects

11) Be mountable on a prepared concrete or other surface with some protection against spills

12) Have the capability of rapid infield changing of the electrode arrangements from monopolar to bipolar and with variation of anode and cathode surface areas.

13) If dc, have the capability of automatic reversal of electrode polarity to prolong electrode life (avoiding reversal with contacts under load)

14) Will include electrical distribution and automated controls for minimum operator attention.

15) Have electrodes that are simple plates that can be changed without special tools or welding

16) Have provisions that allow the system power supply (rectifier) to be capable of maintaining the selected amperage even if the conductivity of the water changes by a considerable degree to avoid excursions or lack of treatment as various changes occur in the water

17) Have capability to run reliably for a long periods at high duty cycle.

Reviewer #3

Target Plume/Area: 100-D Area Chromate Plume

Proposal Title: Field Test Electrocoagulation for Accelerated Clean Up of the Northeastern Chromium Plume in the 100-D Area

Technical Basis of the Proposal:
Electrocoagulation is a viable technology for treating chromate in water. However, its proposed use is in a pump-and-treat system. This is not bad, but it is subject to some of the same limitations as other pump-and-treat systems. The interactions of chromate with soil are minimal compared to uranium or Sr-90, but they do occur. Even a Kd of 0.5 may result in a retardation factor of about 4. Thus, cleanup of the plume may take longer than anticipated. Likewise, if there are solid phase chromate sources (e.g., carbonates), that are not located and removed, cleanup may be very lengthy.

There are some concerns with the chemistry of water produced by electrocoagulation. These should be considered in light of the disposition of the treated water.

Implementation Strategy:

Proposed Performance Metrics:

Summary Evaluation:
Electrocoagulation is viable. There are some issues that should be addressed and a fair comparison to other technologies should be made.

Reviewer #4

Target Plume/Area: 100 Area

Proposal Title: Field Test Electrocoagulation for Accelerated Cleanup of the Northeastern Chromium Plume in the 100-D Area

Technical Basis of the Proposal:
1. The project is based on appropriate and valid science; electrocoagulation is a reasonable choice, as it is a commercially available technology; electrocoagulation produces amorphous lepidocrocite (FeOOH) that can sorb or coprecipitate the chromium; this material then needs to go through a clarifier to separate the solids; Optimization of the system is very complex; not off the shelf, but will need to be designed for the specific groundwater to be treated, which the vendor can do; it is very easy to treat chromium with electrocoagulation; comparison of the performance of this technology to the current ion exchange system in a pilot test will provide good information to select a technology. 2. The likelihood of the desired outcome is very good; the two technologies will be compared to each other in terms of performance.
3. Approach is reasonable and practicable.
4. Were other alternatives examined? CH2MHill is currently doing the alternatives analysis along with cost estimating. If another technology is also shown to be promising for this application, consider adding it to the demonstration.

Implementation Strategy:
- Proposal was written specifically for electrocoagulation, but alternatives analysis has not been completed. If alternative analysis shows that other technologies should be considered and tested, I recommend that the test be expanded to include more than electrocoagulation.
- Sequence and timing appears appropriate given results of alternatives analysis.
- Need a lot of upfront engineering and on-site controls to optimize performance.
- Need to do proof of principle test by sending groundwater, large volume, to the vendor so he can design the system, but still need to do optimization in the field. Changing of electrodes must be easy.
- If re-injection is part of the scheme and the re-injected water has lower TDS, over time the pumped water may also have lower TDS and may affect performance of the system. - - This needs to be examined up front.
- The alternatives analysis and the test itself will provide cost information regarding cost effectiveness.
- Costs for the demonstration are too high, as this is a commercially available technology.

This calls for a commercial skid-mounted system that will be delivered by the vendor and so significant engineering costs may not be incurred ($380K).

Proposed Performance Metrics:
- The project has potential to significantly improve conditions in the 100-D Area, as it can accelerate the cleanup of the chromium plume by expanding the pump and treat system.
- The project attempts to protect the Columbia River in the near term.
- Performance will be measured in the water treatment demonstration. Don't over-promise the length of time to cleanup the plume.

Summary Evaluation:
Overall, recommend the alternatives analysis be completed and then a go decision be made if the electrocoagulation is found to be one of the recommended alternatives (i.e., unless it has a fatal flaw or a significant disadvantage). Go should only be done if cost of the demonstration can be significantly reduced or if money is spent on additional activities such as modeling to optimize the pump and treat system. Thumbs up given results of alternatives analysis. Couple with smart re-injection or disposal at the fire retention basin to accelerate the pump and treat. This would be a similar approach to what was done at the 100-H Cr plume.

Reviewer #5

Target Plume/Area: 100D Area

Proposal Title: Field Test Electrocoagulation for Accelerated Clean Up of the Northeastern Chromium Plume in the 100-D Area

Technical Basis of the Proposal:
Is the project or activity based on appropriate and valid science?
Yes. Use of electrocoagulation to treat metals-contaminated waters in subsurface environments is relatively well-established. The major objective of the EC treatability test is to determine if the process is a viable technology for treating the chromium plume such that it could be used to aggressively cleanup the northeastern chromium plume in the 100D Area.

What is the technical likelihood of the stated-desired outcome? Very good. Numerous applications of this technology have demonstrated that it successfully removes metals and insoluble inorganics from aqueous waste streams. Concerns remain, however, regarding (i) lack of examination/identification/comparison of alternatives; (ii) residual solids characteristics and how they will be both separated from the treated water and disposed; (iii) effect of greatly increased pumping rates (has this been properly vetted in terms of ability to pump from this formation at this higher rate, regardless of the number of wells?); (iv) lack of details on performance metrics for success in terms of pump and treat operations (e.g., evaluation of potential for rebound effects); (v) potential for formation of an impermeable oxide film on the cathode leading to loss of efficiency; (vi) costs associated with electrode replacement, residual water treatment, solids (sludge) disposal; (vii) costs allotted to project management and engineering hours noted in the budget ($100k and $350k, respectively, appear rather high, and is not fully justified within the proposal); and (vii) no quantification of operating costs (especially in terms of energy costs).

How does the project fit in with the totality of proposed activities for the target contaminant/plume? This effort represents an integral component of an overall systems-based approach to remediate the chromium plume in the 100D area. Specifically, this effort is geared towards enhancing the current pump and treat system by eventually replacing the ion exchange treatment method with electrocoagulation. immobilization of chromium in the ISRM plume by circulating a strong reductant, calcium polysulfide, in the aquifer. Additional projects include (i) reinforcing (or repairing to some degree) an existing insitu redox manipulation (ISRM) barrier placed in the 100D area in 1999; (ii) immobilization of chromium in the ISRM plume by circulating a strong reductant, calcium polysulfide, in the aquifer; (iii) location of the chromium sources in the 100D Area; and (iv) remediation of waste sites along the Columbia by 2012 through the River Corridor. This suite of proposed activities is each oriented towards generating a reduction environment. While good, this proposal and each of the other three chromium-plume related proposals, would greatly benefit from direct comparison with alternative methods regarding technical feasibility and especially cost.

Is the proposed approach reasonable and practicable?

Yes, if the unit costs are competitive with other solutions.

What are the risks or key uncertainties in the proposed action(s)?
Risks/uncertainties primarily relate to the efficiency and longevity of treatment method and associated costs.

Are there clear examples of alternative ideas or proposals that should be considered?
Yes. Pump and treat via ion exchange resin has been successful in the 100D area. Should perform cost analysis to compare pump and treat cost with expanded ion exchange resin treatment system vs. employment of electrocoagulation system.

Implementation Strategy:
Is the sequence and timing of activities appropriate?
Yes.

Can the technology be implemented cost-effectively?
Maybe. A part of this proposed effort is to estimate costs per gallon treated and mass of hexavalent chromium removed (considering cost of equipment, materials, utilities, chemicals, waste handling, management and operation and maintenance).

Is the budget and level of effort appropriate for the proposed work?
Costs allotted to project management and engineering hours noted in the budget ($100k and $350k, respectively, appear rather high, and is not fully justified within the proposal); and (iv) no quantification of operating costs (especially in terms of energy costs). Further, this effort/amount should also be justified relative to other expansion of the current ion exchange resin treatment system.

Proposed Performance Metrics:
Does the proposed project or activity represent a significant improvement compared to the baseline?
Yes. The current baseline technology employs pump and treat with use of ion exchange resin for treatment. Electrocoagulation possesses the potential to greatly increase the pumping rate in the 100D area, thus accelerating plume remediation.

Does the project improve the protection of the Columbia River now or in the future?
Yes, this effort will directly improve the protection of the Columbia River by permanently reducing the extent of the chromium plume.

Are there measurable parameters that would document performance? Yes. Stated performance objectives include: (i) demonstrate that EC can reliably reduce hexavalent chromium levels to <20 ppb prior to injection back into the aquifer; (ii) evaluate byproducts of the system to establish waste disposal requirements; (iii) determine the efficiency of hexavalent chromium removal in the groundwater plume; (iv) demonstrate operational reliability and safety of the system; (iv) estimate costs per gallon treated and mass of hexavalent chromium removed (considering cost of equipment, materials, utilities, chemicals, waste handling, management and operation and maintenance); and (v) measure operational data (e.g. pressure and flow) to support scale up of the EC system.

Are these included in the proposal?
Yes.

Summary Evaluation:
Good proposal oriented towards achieving accelerated reduction of contaminant plume in the 100D Area. Strengths include (i) employment of electrocoagulation, a well-established technology for removal of metals and insoluble inorganic materials from aqueous solution; (ii) use of a system that can be remotely operated with fairly minimal maintenance requirements; (iii) potential for residual reduction capacity with hydrogen gas and Fe^{2+} residual; (iv) potential for greatly-accelerated reduction in chromium plume; and (v) potential for reduction in overall remediation costs. Concerns include (i) lack of examination/identification/comparison of alternatives; (ii) residual solids characteristics and how they will be both separated from the treated water and disposed; (iii) effect of greatly increased pumping rates (has this been properly vetted in terms of ability to pump from this formation at this higher rate, regardless of the number of wells?); (iv) lack of details on performance metrics for success in terms of pump and treat operations (e.g., evaluation of potential for rebound effects); (v) formation of an impermeable oxide film on the cathode leading to loss of efficiency; (vi) costs associated with electrode replacement, residual water treatment, solids (sludge) disposal; (vii) costs allotted to project management and engineering hours noted in the budget ($100k and $350k, respectively, appear rather high, and is not fully justified within the proposal); and (vii) no quantification of operating costs (especially in terms of energy costs).

Reviewer #6

Target Plume/Area: Chromium Plume/ 100-D Area

Proposal Title: Field Test Electrocoagulation for Accelerated Clean Up of the Northeastern Chromium Plume in the 100-D Area

Technical Basis of the Proposal:
See Summary

Implementation Strategy:
See Summary

Proposed Performance Metrics:
See Summary

Summary Evaluation:
This proposal was outside my area of technical expertise so I will only offer a few general comments about the proposal and the discussion of the proposal by the experts during the panel review. From my perspective, the proposal was well written and well thought out. I thought that the project seemed realistic and useful and that it should be funded at some level. However, I thought that the cost of the project was high, especially the $380,000 in unspecified "engineering hours. These general impressions were consistent with the discussion between the experts at the panel review. There was a general consensus amongst the panelists that the proposal was worth funding, but probably at a significantly lower level than the requested $2,075,000. The comments of Professor David Cocke during the panel review seemed to be especially constructive and I would rely heavily upon his recommendations. I would also look into trying to contract his company (or Lamar University) to build the electrocoagulation system. It was clear from the discussions that the success of the project will be critically dependent upon the expertise of the contractor who designs and builds the system.

Reviewer #7

Target Plume/Area: Cr / 100 Areas

Proposal Title: Electrocoagulation to increase water treatment throughput

Technical Basis of the Proposal:
General

-- This project is generally consistent with previous peer reviews and recommendations. It fits in to a systematic "blended" approach to the challenge of Cr near the Columbia River. The proposal provides a good descriptive justification of the need for source identification and I support that goal entirely.

Pretty good and appropriate use of and interesting and underutilized water treatment technology.

Electrocoagulation works through a process of electrically induced corrosion of closely spaced plates of sacrificial electrodes. The resulting solution in the interpolate spaces can be tailored to the needed conditions by pretreatment and by selection of the electrode material. The goal is to generate a floc of electrode metal precipitates that incorporate the contaminants. Secondary waste volumes tend to be less than traditional water treatment (e.g., alum addition and settling) and more than column treatments such as ion exchange.

Previous literature shows that this process is effective for Cr (but almost always applied to high concentrations such as metals plating waste). Electrocoagulation should theoretically be viable for lower concentrations and the cost per 1000 gallons is not primarily dependent on initial contaminant concentration.

The water from the process is likely to be reducing and alkaline. The characteristics of the effluent might be manipulated so that if re-injected upgradient (or infiltrated in the vadose zone), the treatment system might work synergistically with the other proposed treatments in the area.

Previous cost comparisons between electrocoagulation and ion exchange have been favorable to electrocoagulation. But, the labor for electrocoagulation is much greater and the labor cost rate assumed in those analyses was not consistent with DOE sites. A better cost projection ($/1000) using Hanford labor conditions and more detailed information from potential vendors is recommended to confirm that this is an appropriate activity.

In terms of costs for this technology test, the costs appear somewhat high – it is a known method where prepackaged units could be mobilized and tested – systems need versatility and adjustability built in. Selection of electrode material and pretreatment, optimization/minimization of labor, etc. could be developed with minimal engineering and relying on and RFP to qualified vendors. The proposed cost of about 2 million is 20% of the overall supplemental funding package and would be a very high treatment cost ($100s per 1000 gallons) at a flow rate of 50 gpm. These numbers don't make this compelling and the costs should be evaluated.

Implementation Strategy:
Schedule is generally reasonable. It may make more sense to use the supplemental money to do some up front legwork and seed the initial setup of a system to actually meet the goals of the project!

Proposed Performance Metrics:
Little detail here – but straightforward – should be in terms of increased flowrate/throughput and concentration reduction.

Summary Evaluation:
With a few caveats, I liked this proposal.

Reviewer #8

Target Plume/Area: Northeastern Chromium Plume/100 D Area

Proposal Title: Field Test Electrocoagulation for Accelerated Clean Up of the Northeastern Chromium Plume in the 100-D Area

Technical Basis of the Proposal:
Is the project or activity based on appropriate and valid science?

The process that is proposed is electroreduction of hexavalent chromium to trivalent chrome followed by electrocoagulation of the trivalent chrome species. Electrocoagulation reactions have been known for many years and have a solid scientific basis.

The reduction and coagulation steps would take place in an AC or DC electrocoagulation system. A DC system is less complex in terms of the electrode configuration and system operation. While the AC system will provide more reliable operation in systems that are subject to oxide coating of the cathode in the system.

The reduction of hexavalent chrome occurs via a ferrous iron reduction where the ferrous iron is liberated from the sacrificial electrode and reacts with hexavalent chrome to form either chromite ($FeCr_2O_4$) or chromium hydroxide ($Cr(OH)_3$) solids as well as iron hydroxide solids. Some adsorption of additional chromium species would be expected on iron or aluminum hydroxide complexes that would be formed as part of the reactions within the treatment system. (Kongsricharoern and Polprasert, Wat. Sci. Tech., Vol. 34, No. 9, pp. 109-116, 1996. and (Latuzt, Jacobs, and Guertin, Chromium (VI) Handbook, CRC Press, pp. 477-489).

The electrocoagulated wastewater would then be directed to a clarifier where the suspended solids will be separated from the treated water. The use of a polymer coagulant to enhance coagulation of the solids formed prior to clarification is recommended to ensure good solids separation occurs in the sedimentation step of the process. (Latuzt, Jacobs, and Guertin, Chromium (VI) Handbook, CRC Press, pp. 477-489)

Data on the treatment of wastewaters from plating operations indicates that the hexavalent chrome, and in some cases total chrome concentrations of 20 ppb can be approached using this technology.

What is the technical likelihood of the stated-desired outcome?

The desired outcome is to expedite treatment of the chromium contaminant plume by increasing the pump and treat system capacity using electrocoagulation to remove chrome from the extracted ground water. The goal is to reduce the hexavalent chromium concentration in the groundwater plume to below 20 ppb over a 6 to 7 year period.

Achieving the desired outcome will be contingent on the electrocoagulation system being able to reliably treat the extracted groundwater to a chromium concentration of less than 20 ppb. Literature and available data suggests that the hexavalent chromium goal should be achievable in the effluent from an electrocoagulation system. Overall the technical likelihood of meeting the desired goal is high.

Based on the proposed flow rates and potential treatment efficiency for the EC system a 500 gallon per minute EC treatment system will remove chromium at a rate that will reduce the overall mass of chromium in the groundwater plume at a rate that should make the cleanup objectives possible in the timeframe stated. However, as the chromium plume is reduced the rate of chromium mass removal will be reduced. At some point the hydraulic withdrawal of the plume will become the governing factor in the speed of the cleanup.

How does the project fit in with the totality of proposed activities for the target contaminant/plume?

Is the proposed approach reasonable and practicable?

The use of electrocoagulation appears to be a reasonable technical solution for the treatment of chromium from the groundwater. The treatment process should have relatively low chemical addition requirements and should have predictable maintenance expenditures.

What are the risks or key uncertainties in the proposed action(s)?

Risks and uncertainties:

Increased power costs due to increasing electrical costs. Since the process is based on electrical current passing through the extracted water to induce treatment increases in electrical cost will have a direct influence ion operating costs.

Sludge production that is greater than expected from supplier claims. Some literature cites a 4 fold increase in sludge production using electrocoagulation over sulfur based reductants. (Patterson, Industrial Wastewater Treatment Technology, Butterworth Publishers, 1985, pp55-75)
Sludge classification will have a direct impact on operating costs. If significant amounts of hexavalent chrome are adsorbed onto iron or aluminum hydroxide floc they may not pass TCLP test and could therefore be classified as a hazardous waste.

The presence of chlorides in the extracted water has the potential to cause the formation of chlorinated organic compounds via reactions with organic compounds in the water.

The presence of cyanide in the extracted water could cause the formation of ferrocyanate compounds if a sacrificial iron electrode is used in the electrocoagulation process.

Inherent to the process are the formation of oxygen and hydrogen via electrolysis of water. Hydrogen is a flammable gas and concentration of hydrogen will need to be minimized by providing adequate ventilation for the process.

Treated water may require polishing to reach the desired hexavalent chrome concentration. Polishing may include sand filtration to remove particulate not removed in the settling process or ion exchange to remove dissolved components not treated in the EC process.

Changes in water chemistry may change the EC system's ability to remove hexavalent chrome. Such changes may occur as the groundwater quality improves.

EC will result in changes to the conductivity of the source water. Changes to the conductivity below 200 to 300 uS/cm may require that a conductivity enhancement step be added to the process. This would involve injecting a salt solution into the extracted water to increase solution conductivity.

Are there clear examples of alternative ideas or proposals that should be considered?

Conventional chemical reduction using a sulfur based reducing agent and hydroxide precipitation of the trivalent chromium. The amount of chromium in the extracted water is not high compared to wastewater applications using chemical treatment. Although suppliers argue that sludge production using EC is lower than for chemical precipitation systems some literature disputes this claim (Patterson). The capital cost for a treatment system using chemical reduction and precipitation of chrome is likely lower than that of a similarly sized EC system. This type of system has been proven to be effective and economical in the past. A side by side comparison on the two processes would provide a useful comparison and provide good justification for using one system over the other.

Consideration should be given to incorporating a polishing system into the EC pilot. This may be a necessary step in the process if the EC process cannot meet the treated water targets. Polishing may include:

Sand filtration of EC clarifier effluent to remove non-settleable solids from the treated water.

Using IX as a polishing step to treat EC effluent.

Using activated carbon as a polishing step to treat EC effluent

Implementation Strategy:
Is the sequence and timing of activities appropriate?

The sequence of activities appears to be appropriate.

Can an EC system designed to treat 50 gpm of groundwater be delivered in 8 weeks?

Contact with supplier of EC equipment indicates that delivery on order is on the order of 12 to 14 weeks plus shop drawing approval.

A parallel plate clarifier will have a delivery of 16 to 20 weeks including shop drawing approval.

A plate and frame filter press has a typical delivery of 16 to 20 weeks including show drawing approval.

The schedule for procurement of the EC system equipment, clarifier, and sludge press do not appear to be consistent with typical equipment delivery timelines.

Can the technology be implemented cost-effectively?

Capital costs for an EC treatment system are probably slightly higher than for a similarly sized chemical reduction system but should be lower than the current ion exchange system.

Operating costs will be highly dependant on electrical costs and on sludge disposal costs. Technology suppliers indicate that the sludge generated by the process will be classified as a non-hazardous waste material. The hazardous nature of the sludge material may be contingent on multiple components in the extracted water stream. Since the EC process is not selective for metal removal it would be prudent to fully investigate the classification of the sludge material from the EC process. If this sludge does not pass a TCLP test and the sludge is classified as hazardous waste the cost for sludge disposal will govern the cost effectiveness of the treatment technology.

The EC treatment systems would be modular such that capital expenditures can be phased in as additional units are required to increase the system capacity.

Is the budget and level of effort appropriate for the proposed work?

The equipment budget (mechanical and electrical) appears to be reasonable for the equipment and installation labor required to implement a 50 gpm pilot unit.

The overall budget seems higher than would be expected for a 6 month pilot test of a skid supplied piece of equipment.

Sludge disposal costs for the process seem to be quite high for a six month pilot study.

The chemical costs for a process that should minimize the use of chemicals seems high at $100,000 for the six month pilot.

The engineering costs for the project appear to be quite high for a system that will essentially be a skid mounted supply package from an EC supplier.

Proposed Performance Metrics:
Does the proposed project or activity represent a significant improvement compared to the baseline?

Based on the information provided the reduction of chromium levels in the extracted water from the pump and treat system in the 100D area will improve the effectiveness of the current ion exchange pump and treat systems.

Does the project improve the protection of the Columbia River now or in the future?

If the electrocoagulation system can be shown to be an effective treatment technology there will be a reduction in the impact of chromium from the Hanford Site, 100-D area on the Columbia River.

Are there measurable parameters that would document performance?

The system is being developed to remove chromium from extracted groundwater. All parameters typically sampled in the groundwater from the 100D area should be sampled for in the pilot test to determine if any changes to other constituent parameters are observed.

Sludge volume and sludge classification should be confirmed.

Base operational electrical consumption and peak (start-up) electrical consumption should be monitored and logged to determine if there is a change in operational characteristics over time. This will establish if the electrodes are experience oxide deposition which can reduce system efficiency.

Changing the water chemistry by blending extracted water with treated water to simulate cleanup results will be useful in order to develop a long term understanding of the treatment system operation in the future as groundwater treatment and the water chemistry changes are observed.

Sacrificial electrodes should be weighed on a regular basis to determine the rate of decomposition and provide an estimated rate of replacement

Are these included in the proposal?

A detailed list of operational and chemical parameters to be analyzed/recorded is not included in the proposal.

The USEPA Environmental Technology Verification program has developed an evaluation protocol of electrocoagulation treatment including monitoring and sampling requirements. This document provides testing and operating procedures for verifying the performance of an electrocoagulation treatment system. (Environmental Technology Verification Program for Metal Finishing Pollution Prevention Technologies Verification Test Plan for the Evaluation of

Kaselco Electrocoagulation Treatment System, Concurrent Technologies Corporation, November, 2001.)

Summary Evaluation:
The investigation of an electrocoagulation treatment system for use in the pump and treat system at the Hanford 100D area Northeastern plume appears to be a technically viable approach to reducing the chromium plume.

There are significant questions regarding the efficiency of the EC system that will require an extended treatability test to prove the system can provide long term reliable chromium removal.

The schedule proposed for the implementation of the process is reasonable but some consideration should be made for a longer lead time for equipment delivery of major equipment items.

APPENDIX I

Inject Micron-sized Iron into the Deteriorating Portions of the ISRM Barrier

Target Plume/Area: Chromium (Cr) / Hanford 100-D Area

Proposal Title: Inject Micron-sized Iron into the Deteriorating Portions of the ISRM Barrier

Proposal Reviewers: Brian Looney, Todd Anderson, David Cocke, Miles Denham, Mark Fuhrmann, Dawn Kaback, Gene LeBoeuf, Bruce Wielinga.

Summary Evaluation:
The panel supports the project, but provides specific recommendations related to design of a more detailed workplan that addresses issues and uncertainties documented below. Primary issues and uncertainties relate to delivery of zero valent iron (ZVI), presence of co-contaminants and byproduct generation, and longevity. Establishment of specific project objectives and metrics to measure performance must be developed. The panel believes the project fits well as part of the systems approach to reduce chromium contamination reaching the Columbia River. The fact that this project builds upon the existing infrastructure of the ISRM is beneficial. Re-scope the laboratory work to answer questions related to issues and uncertainties and then rapidly demonstrate it in the field to test proof-of-principle.

Technical Basis of the Proposal:
The panel generally supports amending the existing ISRM barrier by injecting micron-sized ZVI in an aqueous polymer carrier within targeted intervals where breakthrough has occurred. However, the panel recognizes key issues, identified below, that remain to be addressed before implementation.

The panel believes the project is based on valid and appropriate science; ZVI is a potent reductant providing additional reducing capacity to mend the current ISRM barrier within targeted intervals that have been reoxidized. The concept of delivery within an aqueous polymer is novel. The concept is viable. The fact that this is part of a systems approach for the 100-D Area and that it builds upon the existing ISRM was well supported by the panel.

General technical issues are described below.

Delivery of the ZVI to appropriate locations within the aquifer remains a key uncertainty in assessing its performance. This uncertainty is impacted by the heterogeneity of the aquifer. Delivery of the ZVI is subject to the same vagaries of subsurface flow as was the dithionite.

- Potential settling of the ZVI at the base of high-conductivity intervals where injection occurs may significantly impact performance. Some method for monitoring needs to be developed.
- Performance monitoring of ZVI delivery needs to be better developed. Consider drilling of monitoring points at various distances from the point of injection. Consider use of additional

technologies such as borehole geophysics and cross-borehole geophysical tomography to monitor delivery.
- Consider delivery of a range of ZVI particle sizes to better mimic the natural porosity within the aquifer and potentially save money because the specifications for sizing will be less stringent.
- Introduce the ZVI into the aquifer during the low river stage.
- Introduction of a large number of pore volumes of fluid during injection could cause the spread of Cr-contaminated water and could impact the performance monitoring scheme significantly. Early monitoring results could easily be skewed by this effect.

The presence of “co-contaminants” that are also reduced by ZVI and the generation of byproducts must be considered and monitored. Consider all geochemical impacts.
- Assess the potential for ZVI to convert nitrate to ammonia, which could impact a variety of ecological receptors. A program for monitoring nitrate must be developed.
- Assess the potential for generation of high pH, which could impact downgradient water quality and possibly mobilize other metals. ZVI possesses a high pH between 10 and 14. Consider addition of pyrite to the ZVI to maintain lower pH. Add pH to the monitoring program.
- ZVI may reduce Cr+3 to Cr+2, which is mobile and will maintain a downgradient Cr plume if monitored as total Cr. This will mainly be a stakeholder perception issue, as the Cr+2 should reoxidize to Cr+3 some distance downgradient.
- Introduction of a guar gum polymer into the aquifer may provide a beneficial effect by supplementing the electron donors, but could also pose issues with hydrogen and methane gases that may be produced. The potential for generation of explosive hazard conditions should be examined.
- Consider elimination of the leaking Fire Retention Basin to reduce oxygen and groundwater flow to the ISRM. One recommendation is possible addition of solid particles of a reductant, such as ZVI or other iron materials.

Evaluate the longevity of the ZVI and don’t over-promise its long-term performance.
- Interferences from ferric iron coatings may reduce the longevity of the ZVI.
- High pH due to ZVI may cause precipitation of carbonates, which may reduce permeability and plug the barrier.
- If calcium polysulfide is implemented upgradient, consider the introduction of sulfide and sulfate, which could passivate the ZVI surfaces.

Include an improved description of the work content of the project. The proposal did not adequately describe the work to be conducted.

Other alternatives that could be considered include:

- Injecting iron (II)/iron (III) within the high-K zones of the barrier, if needed, and continuing with dithionite as a reducing agent.
- Better evaluation of the pump and treat system.

Implementation Strategy:

- The sequence and timing seem appropriate, although laboratory work should be directly focused on answering specific questions (e.g., byproducts, pH) and not just scaling up previous work. Further scaling is not needed. After some specific questions are answered by laboratory tests, the project should go to the field.
- The proposed budget costs appear to be high for some activities, especially the portion allocated for developing the test plan for lab work, which is not well described and should not focus on scaling. Costs for lab testing could likely be reduced and better spent in the field to enhance performance monitoring. There is not sufficient information to judge costs of implementation.
- Perform field tests to determine the optimal amounts of polymer and ZVI, by injecting different amounts into different wells. Consider alternate injection/extraction schemes, to determine the appropriate amount of fluid to use during the injection to ensure delivery of the ZVI, but also limit the displacement of Cr-contaminated water during deployment.
- Clarify the location and philosophy of the ZVI injection.
- Consider using a dipole deployment to direct the barrier amendment and minimize the uncontrolled spread of groundwater during the deployment of pore volumes.
- Consider possible use of FLUTe system or redo of EBF in problem wells to identify target zones. This process was not explained in the proposal.
- Implement a robust performance monitoring system. Establish specific objectives that can be measured.

Proposed Performance Metrics:

The panel generally agrees the proposed performance metrics are good but need more specifics.

- Outline performance measures so they clearly describe if goals/objectives are being met. Clarify the exit strategy (i.e., when to claim success). For example, specify concentrations of down-gradient parameters that will indicate success. Don't over-promise performance.
- Develop a robust monitoring program to measure near-term and long-term impacts.
- Define a target for the lifetime of the treatment zone.
- Account for the relatively low Cr concentration during deployment, caused by the injected fluids displacing contaminated water up-gradient and down-gradient.
- Monitor for pH and associated byproducts in the groundwater and the river.
- Describe use of pump and treat system as a back-up/contingency treatment plan.
- Conduct monitoring frequently near the injection site, and install additional monitoring points away from injection sites to determine the radius of influence of the ZVI. Consider post-injection coring to monitor performance.

Reviewer #1

Target Plume/Area: Chromium/Hanford 100D Area

Proposal Title: Inject Micron-sized Iron into Deteriorating Portions of the ISRM Barrier

Technical Basis of the Proposal:

Is the project or activity based on appropriate and valid science?

Yes. Zero valent, micron-sized iron is an effective agent for treating/reducing contaminant metals insitu. This approach has been documented in numerous private industry examples and several research projects.

What is the technical likelihood of the stated-desired outcome?

Injection of zero valent iron into those sections of the existing barrier should provide more available reductant to augment reactive capabilities in those areas of the barrier that appear to be lacking reductive capacity. However, placement of the iron into the subsurface will still be subject to the same vagaries of subsurface flow as the previous dithionite solutions. A polymer that will be injected with the iron may facilitate incorporation of the iron into the matrix material and these attributes should be thoroughly investigated with sediments collected from the site. It is likely that the injected iron will have some impact on Cr(VI) concentrations but how big of an impact will ultimately be determined only upon deployment.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable?

The ISRM barrier will continue to play an important role inhibiting Cr(VI) transport in this area. This is a reasonable approach to "mending" the existing barrier. Zero valent iron injection will immediately boost the reduction potential of the barrier.
Is dithionite re-injection not also a possibility?

What are the risks or key uncertainties in the proposed action(s)?

Zero valent iron produces extremes in pH over time that may pose a downgradient threat. The pH change is related to the corrosion (reduction) of the injected iron particles. Also, substantial hydrogen is developed within zero valent iron barriers. In some instances that can be an explosive hazard for wells near the barrier. Also, zero valent iron barriers are subject to the same loss in reactivity over time as other reactive barriers. In fact, numerous zero valent iron barriers need refreshment from time to time. Is there a refreshment plan for this barrier? If zero valent iron can be shown to have an impact in on mending the ISRM barrier will it be added to the entire barrier in later proposals?

Are there clear examples of alternative ideas or proposals that should be considered? <u>If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations</u>)

Possible alternatives: More dithionite flushing. Was refreshment of the ISRM part of the original workplan for the barrier or was the barrier designed with only a single dithionite flushing? Is dithionite not a viable alternative because of its "presumed" failure in the ISRM? The proposal indicates the barrier failed not because of dithionite but because placement of the solution could not be guaranteed in the heterogeneous subsurface.

Implementation Strategy:
(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)
This is a reasonable approach to mending the barrier other than re-flushing the subsurface with dithionite. Addition of zero valent iron will increase the reductive capacity of the barrier if the iron can be placed properly into position. I have my doubts whether zero valent iron will penetrate areas of the subsurface where dithionite originally did not and about the longevity of the reactive iron.

Proposed Performance Metrics:
A monitoring program will need to be developed to document the Cr(VI) concentration both before and long after emplacement of the zero valent iron. Only then can the insitu performance be judged.

Summary Evaluation:
I find this to be a reasonable solution to mending the insitu redox barrier currently in place. A re-flushing of additional dithionite is also a possibility. Addition of zero valent iron will add reductive capacity to the barrier and, assuming that the iron can be placed where it is needed, could have a substantial impact on soluble Cr in the groundwater. However, I do have concerns about the positioning of the zero valent iron (how will placement be verified), the longevity of its reactivity, and the development of extremes of pH within the iron barrier. Will precipitation of mineral rinds due to high pH impair the reactivity of the zero valent iron and how often will the iron need to be replaced?
How does Cr(VI) behave at high pH? Also, what impact will the high pH of the injected polysulfide solutions have on the barrier components and what will be the fate of all this high pH groundwater? Is there an intervention plan if high alkaline waters start to reach the river bank?

I recommend that this proposal move forward.

Reviewer #2

Target Plume/Area: Hanford, 100-D Area

Proposal Title: Inject Micron-size Iron into Deteriorating Portions of the ISRM Barrier

Technical Basis of the Proposal:
(Is the project or activity based on appropriate and valid science? What is the technical likelihood of the stated-desired outcome? How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable? What are the risks or key uncertainties in the proposed action(s)? Are there clear examples of alternative ideas or proposals that should be considered? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)

Is the project or activity based on appropriate and valid science?

The science is appropriate and valid. However there is no scientific justification to choose a singular micron size for the iron particles. A range of particle sizes that would come from intense milling would be more appropriate and cost effective. Passive, insitu reactive barriers have proven viable, cost-effective systems for the remediation of Cr-contaminated groundwater. For example after 8 years of operation, a zero valent iron PRB remains effective at reducing concentrations of Cr from average values >1500 µg L^{-1} in groundwater hydraulically upgradient of the PRB to values <1 µg L^{-1} in groundwater within and hydraulically downgradient of the PRB. (Wilkin et al., Goldschmidt Conference Abstracts 2005 Zero-Valent Metals, A264).

The principle objectives of this proposal are to mend the ISRM barrier and increase its longevity. This will be done by injecting a solution containing micron-size zero-valent iron and shear-thinning polymers, optimized for conditions in the 100-D aquifer, into permeable portions of the ISRM barrier that have lost some or all of their reductive capacity. This is strongly coupled to the CPS project in that increasing the longevity of the ISRM with iron injection should be augmented by the planned upgradient deployment of calcium polysulfide. This will almost immediately remove chromium from a significant portion of the high-concentration area of the plume and form a permeable reactive barrier by reducing the aquifer perpendicular to groundwater flow. After treatment with calcium polysulfide, the groundwater flowing through the ISRM barrier will have lower dissolved oxygen (DO), nitrate, and hexavalent chromium, which will reduce oxidation in the barrier and increase its functional life. This is appropriate and sound science since zero-valent iron (Fe^0) has been used to remediate a wide range of groundwater contaminants (Gillham and O'Hannisin 1994) the potential to produce three electrons for reduction, compared to the single electron produced during Fe^{2+}.

However some attention needs to be paid to the possibility that Calcium Polysulfide injection into ground water is suspected of producing large amounts of sulfate. This can have several effects: sulfate precipitation can plug the pores, sulfate and sulfide might reduce the effectiveness of injected zero valent iron by interfacial passivation and the sulfate may interfere with electrocoagulation unless appropriate counter measures are taken during the EC.

This is further supported by the successful treatability test using CPS technology performed in the 100-KR-4 area in 2005.

What is the technical likelihood of the stated-desired outcome?

There is considerable technical likelihood of the stated-desired outcome of the larger-scale laboratory flow cell experiments and as evidenced by the successful treatability test using CPS technology performed in the 100-KR-4 area in 2005

How does the project fit in with the totality of proposed activities for the target contaminant/plume?

The application of micron sized zero valent iron with CPS technology fits well with the totality of the proposed activities for the target chromium and the plume(s) identified in the 100 D area. The refinement of the location of the Chromium Source in the 100 Areas is appropriate for the application of the CPS technology since it can be directly applied to the most problematic plume areas as well as be used to generally reduce the oxidative capacity and Cr(VI) concentration up-gradient of the ISRM   The application of Calcium Polysulfide is also quite compatible with EC technology if the additional sulfate that results can be effectively handled. Both CPS and EC are chemically related since the goals of the two technologies are to ultimately chemically reduce the Cr(VI) to Cr(III). However, it is yet to be determined if the additional species introduced into the plume water will interfere with the EC process or in the efficiency of the ZVI that is planned.

The project to immobilize mass in the ISRM plume by circulating the CPS, a strong reductant in the aquifer should also create a persistent zone of reduction that will continue to treat chromium under natural groundwater flow conditions and will likely enhance the longevity of the mended ISRM. EM-21 Proposal.

Is the proposed approach reasonable and practicable?

The new, integrated approach to accelerate cleanup of chromium in the 100 Areas is absolutely the most reasonable and practicable approach. The integrated approach of using an insitu reductant, building more robustness in the ISRM’s by micron sized iron injection and using a chemically complementary technology of EC is excellent. Again, there is a need to explore the synergistic aspects of the three approaches as well as the interferences such a surface passivation of the zero valent iron by sulfides and sulfates as well as the interferences in the EC process that might result from the insitu processes.

What are the risks or key uncertainties in the proposed action(s)?

Assuming that the test results are transferable to the field scenarios, there is good support for projecting successful deployment of the ZVI amending materials.

Given the successful treatability test using CPS technology performed in the 100-KR-4 area in 2005 and combining this with large scale flow tests and the lack of noted unexpected consequences there seems to be no obvious risks or key uncertainties. However, it is again recommended that the three processes be examined for both synergisms and interferences.

In addition, since the recommendations for determining the 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 and PRB, methods to deliver the amendment, and reductant mobility and fate are difficult to assess in the plume and beyond the capacity of the current proposals there will be some uncertainties associated with the project that will have to be determined in the field testing of the ZVI micron sized particle injection

Are there clear examples of alternative ideas or proposals that should be considered?

The most important one have already been considered in the TECHNICAL ASSISTANCE PROJECT #33

1) Dithionite
2) Calcium polysulfide (CaS5)
3) Micro-scale iron
4) Nano-scale iron
5) Dissolved iron (e.g. ferrous sulfate)
6) Biostimulants.

With the CPS and microscale iron being chosen for further work the proposed projects are appropriate. So the answer is no, the reasoning given for the choice of the Ca Polysulfide in report "Evaluation of Amendments for Mending the ISRM barrier, Technical Assistance Project #33, Final Technical Solutions Report, DOE" are sound and the project should proceed as planned.

Implementation Strategy:
(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work? <u>If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)</u>

Is the sequence and timing of activities appropriate?

Yes, the sequence is appropriate to the scale and scope or the project.

This schedule assumes that authorization to proceed is received by April 1, 2006 and that any HQ peer review is also completed before April 1, 2006. A more detailed schedule that will control construction activities is proposed to be developed as the project progresses.

Task 1. Perform laboratory work to gather data necessary for field implementation………………April 1 – September 29, 2006

Task 2. Prepare Work Plan and associated documents….October 2 – November 30, 2006

Task 3. Design mixing/injection system………………. December 4 – February 16, 2007

Task 4. Construct mixing/injection system…………...…February 19 – May 18, 2007

Task 5. Inject iron into ISRM wells……………………..May 21 – June 21, 2007

Task 6. Test report…………………………………….June 25 – September 29, 2007

Task 7. Performance Assessment Coring……………….Out year activity, funded by Site

The above tasks are well sequenced and the activities are appropriate.

Can the technology be implemented cost-effectively?

Yes, the contracting of technology implementation appears to be cost-effective.

Is the budget and level of effort appropriate for the proposed work?

Yes.

Proposed Performance Metrics:
(Does the proposed project or activity represent a significant improvement compared to the baseline? Does the project improve the protection of the Columbia River now or in the future? Are there measurable parameters that would document performance? Are these included in the proposal?)

Does the proposed project or activity represent a significant improvement compared to the baseline?

The existing baseline technology for the southwestern portion of the 100-D plume is ISRM (produced by Sodium Dithionite injection), which is the preferred alternative as defined in the 1999 amended 100-HR-3 interim action ROD. The proposed activity represents a significant improvement compared to the above baseline.

Does the project improve the protection of the Columbia River now or in the future?

Yes, the project improves the protection of the Columbia River.

Are there measurable parameters that would document performance?

Yes, these have been identified in the risks and key uncertainties section.

The Field Test Evaluation Report that will be submitted to RL by September 29, 2007 will evaluate the feasibility of applying zero-valent micron-size iron injection in the100 Area aquifer, and evaluate performance, as data permits. This needs to be more specific and delineation of performance needs to be delineated.
Does the barrier performance improve?
Does the pH change?
What other chemicals are produced?

Summary Evaluation:
The science and the technology appear sound and justify proceeding with the seven (7) tasks to mend the Passive Reactive Barrier. The proposal fits well with the integrated plan to improve the protection of the Columbia River. This is a very valuable approach and should go forward. There seems to be more detail on the lab studies (various size particles, effect of polysulfide on iron, pH effects, ammonia generation, etc). Is this, combined with polysulfide or organic injection, the most cost effective way as compared against pump and treat. Clear consideration needs to be given to the location of where the ZVI is going to be located. In addition, a range of particle sizes and shapes that would come form intense milling should be considered to give the best coverage of the variation in pore sizes and shapes of the geologic materials to be infiltrated with the ZVI.

Reviewer #3

Target Plume/Area: 100-Area Chromate Plume

Proposal Title: Inject Micro-sized Iron into Deteriorating Portions of the ISRM Barrier

Technical Basis of the Proposal:
Potentially viable. Biggest problems are engineering (getting particles where you want them), longevity, and collateral effects of zero-valent iron (ZVI).

ZVI particles will coat with insoluble ferric and ferrous iron phases, reducing the effectiveness of the particles. Thus, longevity is a critical factor.

ZVI will generate high pH (>10) in water passing through the barrier. Does this violate ambient water quality criteria in the river? Does this promote carbonate mineral precipitation that might reduce effectiveness?

It is likely that ZVI will reduce some of the chromate to Cr(II) rather than Cr(III). Cr(II) may remain mobile through the barrier until it finally oxidizes to Cr(III). This is not a significant environmental problem, but the public and stakeholders may be concerned that chromium continues to be present on the downgradient side of the barrier.

Implementation Strategy:
The biggest uncertainty is whether the technology can be implemented effectively. Can the particles be placed where they are needed? The only way to truly find out is to try it.

Proposed Performance Metrics:

Summary Evaluation:
Deployment of ZVI in the ISRM barrier is potentially viable. There are some uncertainties about the chemistry of water that passes through a ZVI barrier that should be addressed.

Reviewer #4

Target Plume/Area: 100-D Area Cr plume

Proposal Title: Injected Micron-size Iron into Deteriorating Portions of the ISRM Barrier

Technical Basis of the Proposal:
The technical basis of this project is the use of fine-grained zero valence Fe as a reduction agent that is injected into failing wells of the ISRM. Because of the density of the particles use of shear thinning fluids allows dispersion of the particles in the subsurface. The proposed work is part of an effort to improve and accelerate "clean-up" of Cr in the 100 area, as some failures in the original treatment wall have been noted. The technical basis is appropriate and sound. The challenge of dispersing Fe particles in the subsurface is well discussed. The use of solid zero valence Fe should be more effective than Fe(II) that was generated by dithionite. In the proposal a 20-fold increase in reductive capacity is noted, it remains to be seen if this works out since surface fouling of the Fe particles will limit their effectiveness, I think.

The discussion in the proposal on the scientific basis of the project gave a good background for the project, but in fact there is no discussion of what will be done. It doesn't look like a section is missing. Laboratory work ($210K in 6 months) is not described. For producing the test plan for lab work and then for the work plan, a total of $230K is requested. I am from a national lab and even to me this seems a bit much.

No information was provided in the proposal regarding details of the work content of the project. Without any details I cannot judge the specific worthiness of this effort.
As part of the overall idea of repairing the ISRM and immobilizing the higher concentration Cr (VI) is appropriate given that portions of the original wall are unable to remediate the high concentrations they are challenged with. The project is reasonable and practicable as it is part of a larger effort to find the sources of Cr, move up-stream to get at high concentrations of contaminants, and repair the current treatment wall.

Implementation Strategy:
The sequence and timing seem OK. Cost seems very high for some activities and are not described. Essentially no details were given regarding the work to be conducted, making judgment difficult.

Proposed Performance Metrics:
The baseline is the ISRM which although it was estimated to last for 20 years based on lab studies, portions of it failed in 10% of that time. This project is intended to repair the failing ISRM and reduce concentrations of aqueous Cr. As such it will be an improvement of the baseline. The performance metric is reduction of Cr(VI) to obtain groundwater concentrations of less than 20 ppb. I suggest another to define a target of some lifetime of the treatment zone: 20 years or 40 years.

Summary Evaluation:
This basic concept of the project is sound. It is probing the state-of-the-art. Unfortunately no details on lab or field work were provided with which to form a judgment.

Reviewer #5

Target Plume/Area: 100 Area

Proposal Title: Inject Micron-size Iron into Deteriorating Portions of the ISRM Barrier

Technical Basis of the Proposal:
(Is the project or activity based on appropriate and valid science? What is the technical likelihood of the stated-desired outcome? How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable? What are the risks or key uncertainties in the proposed action(s)? Are there clear examples of alternative ideas or proposals that should be considered? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)

1. The project is based on appropriate and valid science, as laboratory experiments have demonstrated its effectiveness and the technology has been utilized in permeable reactive barriers in the field for more than ten years; however some issues exist related to delivery (including the effects of aquifer heterogeneity) and long-term effectiveness; this recommendation of augmenting the existing ISRM by targeting high permeability zones with zero valent iron came as a result of two expert panel reviews in 2004. It appears that heterogeneity, preferential pathways especially near the water table have contributed to the deterioration of the ISRM. Because zero valent iron is such a strong reductant, it was recommended for mending the barrier. Due to its high cost, it is recommended for treatment of specific intervals within the aquifer and not to be applied throughout the entire aquifer. Heterogeneity is the biggest issue. The delivery issue is related to zone of influence (how will they monitor this?) I recommend installation of monitoring points at different distances, e.g., 5' and 10', etc., from the injection well. Could they use some sort of geophysical borehole logging or cross borehole tomography to monitor the transport and fate of the ZVI?). There is also a potential issue related to settling of solid particles at the base of the preferential pathways; these pathways likely have very high flow velocities and the groundwater may not have sufficient time to interact with the ZVI that has settled to the base of the preferential pathway. Another potential issue is the likely production of ammonia due to great reductant capability of ZVI. They should monitor for ammonia. ZVI may also create Cr^{+2}, which is mobile like Fe^{+2}, but not toxic. Monitoring through analysis of total chromium in the vicinity of the treatment zone might present a complicated picture. I would anticipate that downgradient it would be oxidized to Cr^{+3} and be immobilized by coprecipitation on ferric oxyhydroxides. Addition of ZVI to the aquifer might also produce high pH, which may not meet ambient water quality standards. The natural pH of ZVI = 11 to 12. pH should also be added to the performance metrics. They should consider addition of pyrite with the ZVI to maintain lower pH.
2. It is not clear which type of iron will be injected. Two types, S-3700 colloids and ARS micron size iron, are mentioned in the proposal. Title of proposal says micron sized.
2. The likelihood of the desired outcome is very good, but issues described above could impact performance. A more detailed plan must include methods for performance monitoring of the delivery of the ZVI.

3. Approach is reasonable and practicable, but detail is needed to understand how the performance will be monitored.
4. Key risks and uncertainties relate to the delivery (how far into the formation does the iron travel), long-term effectiveness (how long will the iron last?). The purpose of this project is to determine answers to these two questions.
5. Alternatives that were examined included calcium polysulfide (subject of another proposal), re-injection of dithionite, bioremediation upgradient to remove the co-contaminants (oxygen and nitrate which utilize the bulk of the reductant).

Implementation Strategy:
(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)

1. Additional laboratory tests are not needed, unless a small study is done to look at byproducts. This project needs to go quickly to the field. Optimization of the amounts of polymer and ZVI can be done through field tests, where different amounts are injected in different wells (3 are being injected).
2. Injection of large volumes of fluids (30 pore volumes) may complicate the measurement of the performance of the system. Will organic byproducts from the guar gum present an issue? (This can possibly be researched in the literature because PRBs typically are constructed with guar gum.) How was the volume of 30 pore volumes determined? Need to demonstrate that this volume is really appropriate. May want to consider testing an injection/extraction scheme in one of the wells; this approach could remove some of the injected fluid, while hopefully leaving the ZVI in the aquifer. Might also be useful in the monitoring of the delivery of the ZVI.
3. Questions exist about details of the planned implementation: will electronic borehole flowmeter data be used to target the zones for injection? These details are missing from the proposal.
4. Consider addition of a range of grain sizes of ZVI, so that it can access a variety of pore diameters. Less stringent grain size requirements might significantly reduce the cost of the ZVI. Other vendor sources should be explored.
5. The budget and level of effort is appropriate, but could be reduced if laboratory work is omitted or funds could be allocated to more field testing.

Proposed Performance Metrics:

1. The project has potential to significantly improve conditions at the ISRM and thus is positive as it mends the existing system and uses the existing infrastructure..
2. The project attempts to protect the Columbia River in the near term.
3. Performance of the technology will be measured by the current monitoring system. We recommend consideration of monitoring on a more frequent schedule near the site of the

injection, adding additional parameters, and installing closer monitoring points to focus on determination of the radius of influence of the ZVI.

4. Consider possible use of FLUTe system or redo of EBF in problem wells to identify target zones.

Summary Evaluation:
Overall, recommend this technology be implemented. Laboratory task should be re-scoped to measure byproducts (pH and ammonia), addition of pyrite to lower pH, and use of ZVI with a range of grain sizes. A larger scale laboratory test isn't necessary.
Also recommended looking at addition of solid zero-valent iron (possibly mixed with pyrite to maintain pH) in the bottom of the fire retention basin.

Reviewer #6

Target Plume/Area: 100D Area

Proposal Title: 100 D Area Inject Micron-size Iron into Deteriorating Portions of the Insitu Redox Manipulation (ISRM) Barrier

Technical Basis of the Proposal:
Is the project or activity based on appropriate and valid science?
Yes. Use of zero-valent iron to enhance redox barriers in subsurface environments is well-established. This project, however, employs a zero-valent iron polymer solution to assist in the transport and improved coverage of the iron at target locations. The project also employs a well-structured methodology to combine both laboratory analyses and pilot field study.

What is the technical likelihood of the stated-desired outcome?
Good, with concerns remaining regarding targeted injection considering heterogeneity of the subsurface in the 100D area and longevity of residual zero-valent iron given conditions at site (including high phosphate concentrations).

How does the project fit in with the totality of proposed activities for the target contaminant/plume? This effort represents an integral component of an overall systems-based approach to remediate the chromium plume in the 100D area. Specifically, this effort is geared towards reinforcing (or repairing to some degree) an existing insitu redox manipulation (ISRM) barrier placed in the 100D area in 1999. Additional projects include deployment of an electrocoagulation treatment system as part of an expanded pump and treat system, location of the chromium sources in the 100D Area, and remediation of waste sites along the Columbia by 2012 through the River Corridor. This suite of proposed activities are each oriented towards generating a reduction environment. While good, this proposal and each of the other three chromium-plume related proposals, would greatly benefit from direct comparison with alternative methods regarding technical feasibility and especially cost.

Is the proposed approach reasonable and practicable?
Yes.

What are the risks or key uncertainties in the proposed action(s)?
Risks/uncertainties include: (i) is the conceptual model for premature breakthrough to the ISRM barrier correct?; (ii) site heterogeneity causing difficulty in locating and injecting iron polymer solution in correct locations; (iii) longevity of zero-valent iron given site conditions; (iv) potential mobilization of naturally-occurring arsenic; and (v) estimate of the number of wells required and its impact on the overall cost of the project.

Are there clear examples of alternative ideas or proposals that should be considered?
Yes. Pump and treat has been very successful in the 100K area. Should perform cost analysis to compare pump and treat cost vs. ISRM and polysulfate injection vs. other alternatives.

Implementation Strategy:
Is the sequence and timing of activities appropriate?
Yes.

Can the technology be implemented cost-effectively?
Yes, if the conceptual model is correct.

Is the budget and level of effort appropriate for the proposed work?
Yes, although again not well illustrated (details missing).

Proposed Performance Metrics:
Does the proposed project or activity represent a significant improvement compared to the baseline?
Yes, to some degree. Use of a polymer-enhanced zero-valent iron provides for enhanced reductive capacity relative to the sodium dithionite-based ISRM.

Does the project improve the protection of the Columbia River now or in the future?
Yes, as a temporary barrier that assists in the "protection in depth" protocol.

Are there measurable parameters that would document performance?
Yes, although the proposal should more explicitly state specifics of these measurements. The downgradient groundwater will be monitored for redox-sensitive parameters including dissolved oxygen, oxidation-reduction potential, iron, manganese, lead, and arsenic. However, this statement does not specifically specify concentrations that will indicate success.

Are these included in the proposal?
Yes.

Summary Evaluation:
Very good proposal. Strengths oriented towards employment of micron-sized zero-valent iron solution to enhance mobilization and coverage in zones of primary interest – high permeability areas, including the coupling of laboratory studies, pilot studies in the field, and coring at the completion of the study. Concerns (i) is the correct conceptual model being employed? (i.e., what level of confidence points to the cause of premature barrier breakdown to heterogeneities in the aquifer, where laterally discontinuous units with high permeability and lower inherent reductive capacity (because of lower iron content) were reoxidized faster than the less transmissive layers); (ii) method of identification of injection and influence of heterogeneity; (iii) concern of locality of calcium polysulfide injection relative to ISRM barrier and zero-valent iron injection; and (iv) risk associated with scale-up from column and wedge-shaped studies regarding delivery effectiveness (this can be addressed by including a means to measure the zone of influence via close vicinity monitoring wells or other means).

Reviewer #7

Target Plume/Area: Cr / 100 Areas

Proposal Title: Inject micron size iron into deteriorating portions of the ISRM barrier

Technical Basis of the Proposal:
General

-- This project is generally consistent with previous peer reviews and recommendations. It fits in to a systematic "blended" approach to the challenge of Cr near the Columbia River.

The project addresses the "failure" (suboptimal performance) of the barrier and proposes amendment with micron sized iron deployed in an aqueous polymer carrier such as a traditional guar gum. Other amendments were considered including nanoiron, dithionite, etc. Follow up testing demonstrated the ability to deploy the iron over relevant scales (with preferential flow in coarse heterogeneities – this is a potential positive since these are the zones of breakthrough)

This project needs to directly address the three previously identified primary causes of barrier breakthrough: 1) physical and chemical heterogeneity within the aquifer, 2) input of competing electron acceptors, such as nitrate, and 3) (specific to dithionite barrier formation) potential limitation of natural iron minerals in the permeable zones . The lifetime estimates for the mending need to account properly for the high nitrate levels. This appears to have been done in the Oostrom 2005 reference.

The project considered ecological and environmental impacts from DO reduction associated with the zero valent iron but did not discuss other important zero valent iron chemical impacts such as the potential for high pH (circa 10 to 14). These impacts could include direct impacts or undesirable geochemical effects such as mobilizing and other metals as alkaline complexes.

A strength of the proposal is that the injection will tend to target/follow the high permeability zones – the same zones that have been shown to be where the dithionite barrier is breaking through – this is one case where heterogeneity is being used to the advantage of the remediation deployment.

Relatively large injection volumes were needed in the column experiments to deploy the iron (e.g., 30 pore volumes). This is a rather large amount of injection and there may be potential for spreading displacing chromium contaminated water for a short period during deployment. Further, the injection fluid will displace both upgradient and downgradient of the injection, so that there will be a period of low concentrations that may not be indicative of performance after the deployment – this may need to be accounted when developing performance measures.

The polymer carrier may will degrade and serve as an electron donor until it is used up – this may supplement the zero valent iron effectiveness and may provide some buffering via CO_2 production.

Better evaluation of alternatives such as pump and treat are needed – include cost, time, etc. Need to consider eliminating leaking basin to reduce driving force and the addition of oxygen to the system.

Cost appears reasonable.

Implementation Strategy:
Schedule is generally reasonable.

A few key details of the deployment were not clearly laid out in the proposal such as the location (or philosophy) of injection. Is there any need for a dipole deployment to direct the amendment through the barrier and to minimize uncontrolled spread of groundwater during many 10s of pore volumes? A dipole option would allow a opportunity for monitoring since the withdrawal of polymer water would contain less iron and allow a mass balance on the iron deposited. Is the injection planned into the barrier, or upgradient? This philosophy should be clarified.

Proposed Performance Metrics:
Some good performance metrics based on previous ISRM experience. Need to consider pH impacts as well and other potential byproducts – ammonia, Cr(II). Need to have a contingency of pump and treat and the basis for implementing.

Summary Evaluation:
Good proposal.

Reviewer #8

Target Plume/Area: Hanford, 100-D Area

Proposal Title: Inject Micron-Size Iron into Deteriorating Portions of the ISRM Barrier

Technical Basis of the Proposal:

Is the project or activity based on appropriate and valid science? Zero-valent iron is a potent reductant that can add additional reducing capacity to the current ISRM barrier. In addition, mending the barrier with micron-scale iron can potentially add additional iron to high-K zones that are hypothesized to be responsible for premature chromium breakthrough. The science that is at the base of this proposal is valid, and may offer an appropriate and cost-effective approach for mending the barrier.

What is the technical likelihood of the stated-desired outcome? This is somewhat uncertain given the highly heterogeneous nature of the aquifer. This testing is design to provide insights into this question. However, the proposal indicates that high permeability zones would be targeted but provides little information on how these zones would be identified.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? The project in theory fits well with the other proposed activities at the site by reducing the flux of chromium to the river while other complimenting technologies are deployed upgradient thus reducing the oxidizing potential and total nitrogen of influent ground water. In addition, it could extend the lifecycle and efficacy of the ISRM barrier that is currently operable and removing chromium mass from the ground water.

Is the proposed approach reasonable and practicable? If proven to be effective, the mending approach is reasonable, and if as effective as initial calculations suggest would greatly extends the life of the barrier and provide a potentially cost-effect means to enhance barrier performance.

What are the risks or key uncertainties in the proposed action(s)? Key risks and uncertainties include the impact of rising ground water pH on the river, the creation of an anoxic plume, and the potential for stoichiometric conversion of nitrate to ammonia. It will be imperative to adequately assess the potential ecological risks (real or imagined) that these possible changes in ground water chemistry will have on the potential ecological receptors.

Are there clear examples of alternative ideas or proposals that should be considered? Other options are emplacement of Fe(II)/Fe(III) within the high-K zones of barrier and continue with dithionite as reducing agent.

Implementation Strategy:

Is the sequence and timing of activities appropriate? Yes, large scale flow cell columns to precede scale-up to field scale pilot testing.

Can the technology be implemented cost-effectively? If proven to be effective and able provide the calculated longevity this could be a cost-effective solution.

Is the budget and level of effort appropriate for the proposed work? Budgetary analysis is better addressed by those familiar with costs typically associate with this type of work at national labs.

Proposed Performance Metrics:
Does the proposed project or activity represent a significant improvement compared to the baseline? Yes. If the technology can extend the life of the barrier by 60 yrs with a single injection this would be a significant improvement.

Does the project improve the protection of the Columbia River now or in the future? Yes, if successful and ammonia does not become a problem.

Are there measurable parameters that would document performance? Not clearly stated in proposal but it is assumed that these would be similar to those previously used for evaluating the effectiveness of the dithionite barrier system. However, addition of metrics to evaluate the actual distribution (e.g. radius of influence) of the iron injected should be considered.

Are these included in the proposal? (see above)

Summary Evaluation:
The primary objective of the work proposed here is to evaluate a technology that will mend the ISRM barrier in the 100-D Area at Hanford. However, ZVI is a highly effective reductant and potentially useful for remediating numerous constituents other than Cr(VI), which is the target of these efforts. If this emplacement technology can be demonstrated in the field at this site it potentially adds an important new tool to the remediation tool box.

APPENDIX J

300 Area Uranium Plume Treatability Demonstration Project: Uranium Stabilization through Polyphosphate Injection

Target Plume /Area: Uranium / Hanford 300-FF-5 Area

Proposal Title: 300 Area Uranium Plume Treatability Demonstration Project: Uranium Stabilization through Polyphosphate Injection

Proposal Reviewers: Dawn Kaback, Todd Anderson, Miles Denham, Mark Fuhrmann, Gene LeBoeuf, Brian Looney, Bruce Wielinga.

Summary Evaluation:
The panel generally supports the proposal with some recommendations and uncertainties that should be addressed. Identified issues and concerns are related to the method of injection and influence of subsurface heterogeneity, longevity of the polyphosphate apatite barrier, approaches to laboratory experiments, geochemical impacts resulting from the injection, and long-term monitoring of the uranium plume. The proposal provides for a combination of laboratory and field investigations that should provide the data required to evaluate the likelihood of successful deployment.

Technical Basis of the Proposal:
The panel generally supports the injection of polyphosphate to directly stabilize uranium concentrations through precipitation of insoluble uranium-phosphate minerals. The panel believes this approach is well studied and is scientifically valid and appropriate. The proposal also provides a good combination of lab and field components.

Technical issues for consideration:

- A more detailed description of how polyphosphate will be injected and dispersed, including impacts of subsurface heterogeneity.
- Include more detailed discussion of alternative methods to mitigate uranium movement.
  - Include results from the EMSP-funded work on redox stabilization as part of the technology selection process or as an alternative technology.
  - Hanford groundwater is supersaturated with calcite and calcite retains significant amounts of uranium, so calcite precipitation should be considered a potential alternative to polyphosphate injection. (Reviewer 3)
  - Bioreduction through the injection of an organic compound as a uranium immobilization alternative to polyphosphate injection. (Reviewers 1, 6)
  - Push-pull testing, as opposed to straight injection; it may improve the understanding of subsurface conditions.
- The concentration of phosphate resulting from the injection as a potential a risk to near-term water quality. (Reviewer 4)

- Evaluate impacts to subsurface geochemistry as a result of the polyphosphate injection:
  - Address the geochemical impact on microbial populations from injecting polyphosphate. Competing reactions involving the injected phosphate, such as stimulated microbial growth, may affect the ability of apatite to stabilize uranium concentrations. (Reviewer 2)
  - Potential for colloidal uranium migration.
  - Potential for phosphate to disperse clay minerals, which could reduce the permeability of the sediments. (Reviewer 2)
  - Identify additional phosphate mineral phases that could form, which are less soluble and may tend to co-precipitate uranium. (Reviewer 4)
  - Address the impacts of mineral weathering and the associated potential loss of uranium.
  - Salting out could affect uranium sorption. (Reviewer 6)
  - Address the potential impacts of various pH ranges on the ability of phosphate phases to sorb uranium. Subtle differences in pH will cause significant concerns about the effectiveness of the process.
  - Address issues related to the potential for phosphate to destabilize autunite. Consider performing autunite precipitation experiments and ramp up phosphate concentrations. These experiments should try to replicate groundwater and other field conditions. (Reviewer 2)
  - Use of blends of different polymer lengths that would spread the release of phosphate over space and time. (Reviewer 6)
  - Conduct long-term (more than three years) evaluation of natural analogues to ensure a more robust understanding of the stability of the injected polyphosphate apatite barrier.
- The proposed approach for the column experiments uses uranium-spiked clean sediment, rather than uranium-contaminated sediment. It is unclear whether the spiked uranium sediment can adequately mimic uranium-contaminated sediment. Consider batch studies as an alternative to column studies, to evaluate the mass transfer and sorption of uranium. In addition, column experiments should include post-mortem analysis. (Reviewers 1, 3)
- Impacts of the water level at different river stages in the approaches for various experiments.
- Use of store and release covers for infiltration in the case of a precipitation event.
- Evaluate the possible economy of scale benefits from testing both the injection of polyphosphate and calcium-citrate-polyphosphate apatite solution for addressing the ^{90}Sr plume in the Hanford100-N Area and the uranium plume in the Hanford 300 Area.
- Potential stakeholder concerns about the longevity of the polyphosphate apatite barrier and long-term stewardship of the Hanford site.
- The Department of Energy-Richland Operations Office should perform a Natural Resource Damage Assessment, since insitu treatment of uranium leaves a possible continuing source of uranium in the Hanford subsurface.

Implementation Strategy:

- Budgeted costs, sequencing, and timing are generally appropriate for the level of work.
- Provide more detail about the development of the field project. A test plot should be large enough and include sufficient number of monitoring wells to determine the efficacy of the process.

- Since 40% of the budgeted cost is for drilling wells for injecting polyphosphate, consider using bore holes and existing wells to significantly reduce costs. (Reviewers 2, 4)
- There may be additional unforeseen costs, such as inadequate well placement or additional drilling, during the transition to the field test.
- The pilot test plan should include a discussion of spatial scales and time.
- Full-scale implementation will require additional testing and design to address outstanding technical issues, such as the impact of subsurface heterogeneity.
- Insitu stabilization of uranium should include long-term monitoring of uranium concentrations, including coring to ensure available uranium is sequestered within autunite in oxidized form. (Reviewer 5)
- Provide evidence that this technology can be implemented and operated cost effectively. Currently this approach is just a "proof of principle" test.
- Consider combining polyphosphate injection with the apatite infiltration in the Hanford 100-N Area, and perform concurrent laboratory tests for uranium and strontium.

Proposed Performance Metrics:

- The proposed performance metrics are reasonable, and the project is a significant improvement on the baseline.
- Performance metrics should be developed for the field test.
- Calcium, phosphate, and uranium should be monitored early and often during polyphosphate injection. (Reviewer 1)
- Simply monitoring uranium concentrations at the river's edge may not be indicative of system performance in the near-term. A more comprehensive monitoring approach should be conducted throughout the uranium plume in addition to monitoring uranium concentration at the river's edge. (Reviewer 4)
- Consider monitoring additional components, such as sodium and phosphate.

Reviewer #1

Target Plume/Area: Uranium/Hanford 300 Area

Proposal Title: 300 Area Uranium Plume Treatability Demonstration Project: Uranium Stabilization Through Polyphosphate Injection

Technical Basis of the Proposal:
Is the project or activity based on appropriate and valid science?
Yes. Polyphosphate injection as a uranium sequestration technique was developed within the EMSP program.

What is the technical likelihood of the stated-desired outcome?
The experimental results of the column experiments with Hanford 300 sediment will yield an estimation of the potential for autunite/apatite formation in native sediments, the ability of precipitated phosphate phases to remove U from solution, and an estimate of the longevity of U sequestration. The pilot test will be an extrapolation of these lab results. It remains to be seen whether the expected results, U concentrations below the EPA MCL, will be achieved insitu.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable?
Polyphosphate injection for the source areas of U contamination seems appropriate if the phosphate phases precipitate where they are supposed to in the subsurface with minimal aquifer plugging. Also, there may be potential mobilization of U off of the sediment upon the initial phases of the phosphate injection. This needs to be taken into account. The column studies with Hanford 300 Area sediments (contaminated?) should show whether a pulse of U could be expected insitu during early P injection.

What are the risks or key uncertainties in the proposed action(s)?
Early mobilization of U could be a potential risk as sorbed U is displaced by the injected high ionic strength phosphate solutions into the subsurface. Also, if precipitation of phosphate solutions does not occur as rapidly as expected, export of P to the river could be an issue. Also, what are the consequences of aquifer plugging in this systems…does it matter?

Are there clear examples of alternative ideas or proposals that should be considered? <u>If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations</u>)
Was bioreduction excluded as a possibility? There are now several field-based tests of bioreduction as an immobilization strategy that simply require injection of a simple organic compound. Bioimmobilization does carry an as yet unknown risk of remobilization should more oxidizing conditions occur later in time. More recent results suggest that if microbial processes can be pushed into sulfate reduction, then continued removal of radionuclides tends to persist. In one field test continued removal has been observed for several years now.

Implementation Strategy:
(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)
The budget is consistent with the level of effort. As the project starts to transition to the pilot test in the field there could be some additional costs that are unforeseen at this time such as inadequate well placement and a need for more drilling etc.

Proposed Performance Metrics:
(Does the proposed project or activity represent a significant improvement compared to the baseline? Does the project improve the protection of the Columbia River now or in the future? Are there measurable parameters that would document performance? Are these included in the proposal?)
The primary concern for performance metrics is during the field test. Analysis of groundwater samples was mentioned during the polyphosphate injection. Ca, P and U concentration should be monitored early and often during P injection. There was mention of recovering cores from the subsurface after the field pilot to determine the position of U-sequestering minerals. This will be important to verify the production of solid P phases, hopefully containing immobilized U, and to assess the overall validity of the project.

Summary Evaluation:
The proposed experiments will provide a reasonable evaluation of polyphosphate injection into the Hanford 300 Area. Column studies with Hanford 300 area sediments and groundwater are key to determining the potential for polyphosphate injection, precipitation of P phases, the removal of soluble U to the EPA MCL, and an estimate of the longevity of U-sequestrating P phases.
I find the laboratory experiments reasonable to the proposed objectives. The field scale pilot test is critical to developing the technique. Care must be taken to identify a suitable injection well and a suitable set of the monitoring wells that will be able to adequately monitor the effect of P injection on the subsurface U concentrations. This is critical to the project to validate the conceptual model and validate the process in the subsurface.
I recommend that this proposal move forward.

Reviewer #2

Target Plume/Area: 300-Area Uranium Plume

Proposal Title: Uranium Stabilization Through Polyphosphate Injection

Technical Basis of the Proposal:
There is a sound technical basis – at high phosphate concentrations uranium phases will precipitate or phases capable of sequestering uranium will precipitate. Using polyphosphates is a clever way to slowly release orthophosphate into an aquifer.

Uncertainties:
0.05M phosphate is 4750 mg/L, an enormous phosphate concentration. If concentrations are really going to be anywhere close to this:

Will ambient water quality standards for phosphate in the river be violated?
Will clay minerals be dispersed, clogging permeability?
Effect on microbial populations?

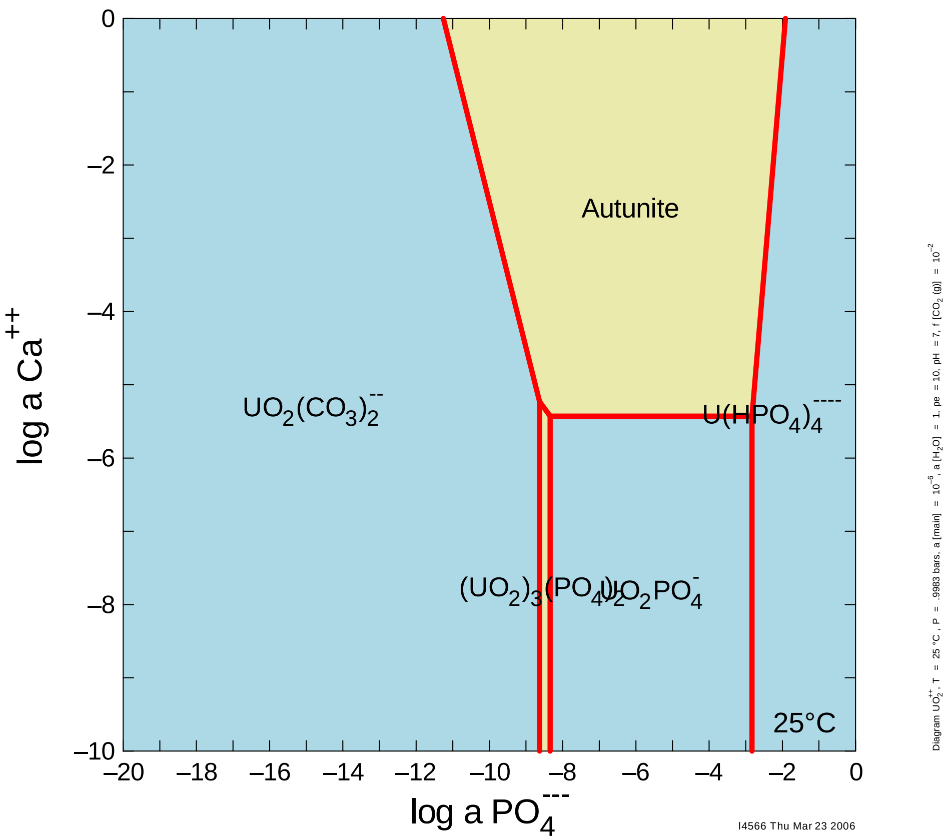
Autunite may actually be less stable at extremely high phosphate concentrations because the phosphate stabilizes U(IV) to much more oxidizing conditions. The attached figure suggests these limitations. This should be investigated, at least through calculations, prior to injecting high phosphate concentrations.

Implementation Strategy:
Much of the proposed work is in the realm of basic science and may not be necessary for this type of treatability demonstration. For example, the pre- and post-field test experiments could be streamlined to obtain only information necessary to deploy and evaluate the technology. For the amount of work proposed the budget is probably reasonable, whether or not they really need to do all of this work is the question.

One budget note: 40% of the total cost is drilling. Could they reduce the number of test holes or use lower cost drilling methods?

Proposed Performance Metrics:

Summary Evaluation:
The idea behind the proposal is sound and should be pursued. However, they could have a successful demonstration with much less work.


Autunite
UO2(CO3)2--
U(HPO4)4----
(UO2)3(PO4)2
UO2PO4-
25°C
log a Ca++
log a PO4---
0
–2
–4
–6
–8
–10
–20
–18
–16
–14
–12
–10
–8
–6
–4
–2
0
I4566 Thu Mar 23 2006
Diagram UO2++, T = 25 °C , P = .9983 bars, a [main] = 10–6 , a [H2O] = 1, pe = 10, pH = 7, f [CO2 (g)] = 10–2

Reviewer #3

Target Plume/Area: 300 Area Uranium Plume

Project Title: Uranium Stabilization through Polyphosphate Injection.

Technical Basis of the Proposal:

This proposal is based on the use of polyphosphate injection into areas of U contamination to reduce the concentrations of aqueous U to 30 ppb. The proposed work will assess the behavior of the polyphosphate reagent with constituents of the groundwater, the formation of autunite and apatite, their efficacy with regard to U retention and finally a field trail of the method. With regard to reacting U with phosphate to precipitate it in one of many forms, the technical basis of the proposal is sound and the overall approach is appropriate. As opposed to the process proposed for the 100 N area in which apatite is to be precipitated to remediate Sr-90, the method here uses long-chain polyphosphates which dissociate by hydrolysis, slowly providing reactive phosphate for the reaction. It is unclear if there are technical reasons for both methods being examined. I see no problem with developing both (probably a good idea).

One key risk is the kinetics of the dissociation of polyphosphate in the groundwater. That is part of Task 2 and it seems like much of this work hinges on how well understood that process is. No data were presented in the proposal (or referenced) to provide an idea if this will take hours, days, or years. An issue that may become important is if the phosphate will stimulate bacterial growth. While the low carbon content of the system makes this unlikely, if reducing conditions are generated, results will be unclear as to whether autunite precipitation or reduction is limiting U solubility. Another concern is what form is U present in the solid phase in the contaminated sediment. It is not clear if the polyphosphate would be injected into “hot spots” to minimize the soluble source term as well as to intercept a plume of aqueous U. If so then surface interaction of the polyphosphate with sorbed or precipitated U needs to be studied. Assumptions are made about what minerals are forming that may not be true and this will very much alter the concentrations of U in solution.

The approach taken in the column experiments is a concern. Instead of using U contaminated sediment, it seems that U will be spiked into clean sediment. Here it is unclear what form U will be in. We don’t know how much U will sorb on the sediment, how long that will take and what forms of solid may be generated. For example, will calcite precipitate and carry U with it? What forms does U take in the contaminated sediment after aging for decades? Given these questions, it seems very important to use the site specific, contaminated soil in the columns and the aqueous U that results. No “post-mortem” analysis of the columns is described. There is a lot to learn from the redistributions of elements in the solid phase of these columns, I am sure. The utility of the tests using increasing flow rate is not clear to me. It is intended to distinguish between desorption kinetics and dissolution controlled release. I suspect that is appropriate for systems that are not mass limited, but here we have small quantities of U or P and it may simply indicate the presence of different solid phases. The long-term behavior of autunite (or whatever forms) and apatite in the saturated zone is presumably poorly understood. Some effort should be made to examine the aging of these phases in the groundwater. The PA sampling for the field study does have post-treatment column studies, that is good.

The groundwater is supersaturated with respect to calcite and calcite does retain significant quantities of U as both U(VI) and U(IV). Would calcite precipitation be a useful strategy?

Implementation Strategy:
The sequence and timing seem OK. However, the pilot-scale plan does not have a discussion of spatial scales and of time. In the implementation schedule about 5 months are given. Is this enough? Cost seems reasonable for this proposal and if the full-scale infiltration works out, very significant saving in money, river quality and PR will be attained.

Proposed Performance Metrics:
The proposed work hopefully will lead to better retention of U than the baseline Yes it should provide improved protection of the river. I think that it may be wise to put a decision point in after Task 2.

Summary Evaluation:
While the overall thrust of the proposed work is appropriate and the basic science behind it is sound, I have concerns as discussed above about the approaches taken to examine the behavior of these materials in the lab studies. Use of actual contaminated sediment is imperative.

Reviewer #4

Target Plume/Area: 300 Area

Proposal Title: Polyphosphate Injection for Uranium Stabilization

Technical Basis of the Proposal:
(Is the project or activity based on appropriate and valid science? What is the technical likelihood of the stated-desired outcome? How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable? What are the risks or key uncertainties in the proposed action(s)? Are there clear examples of alternative ideas or proposals that should be considered? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)

1. The project is based on appropriate and valid science, as uranium is known to be precipitated with phosphate and become relatively insoluble; however some issues exist related to delivery (i.e., heterogeneity), scaling, and long-term effectiveness; possible concern regarding effectiveness under natural pH conditions and presence of carbonate *Have they overlooked impact of microbes? 4700 mg/l phosphate to be injected. Can this impact river quality. Phosphate may disperse clays? Could this cause colloidal migration? What will crystal size be? Too much phosphate can destabilize autunite. May want consider autunite precipitation experiments and ramp up phosphate concentrations. Uranium phosphate phases could form; are they more soluble? Stability could be investigated through natural analogs. Lab tests should be more realistic, too big a stretch to field test; for example, why spiked groundwater and why not real core samples from 300 Area; what about post mortem on columns (do have post test field core analyses).*
2. The likelihood of the desired outcome is fair to good, but issues described above could impact performance.
3. Approach is reasonable and practicable, but must address issues described above.
4. Key risks and uncertainties relate to the delivery, scaling, long-term effectiveness, presence of co-contaminants affecting performance. Is there a possible stakeholder concern about leaving the contamination in place?
5. Alternatives, such as apatite as proposed in the 100 N Area, insitu redox manipulation or soil flushing do exist. Little evidence of how this alternative was selected as compared to other alternatives was presented in the proposal.

Implementation Strategy:
(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)

1. The sequence and timing of activities is appropriate; full-scale implementation will require significant further testing and design especially related to delivery (heterogeneity

and scaling); resources will need to be committed to address this issue. Will need to work out effects of high versus low water.

2. Currently there is not sufficient evidence that the technology can be implemented cost effectively; this project is just a proof of principle test and will require significant further testing, especially related to scale up prior to implementation. The large size of the uranium plume is a concern regarding its implementation and cost effectiveness.
3. Consider push pull testing as opposed to straight injection. This may help improve our understanding of the subsurface conditions at this site.
4. Not sure of the budget proposed, ~$1.7M; recommend using existing wells for injection to reduce $460K of drilling costs through use of CPT or Vibracoring from the year one budget and some reduction in the year 2 budget.

Proposed Performance Metrics:
(Does the proposed project or activity represent a significant improvement compared to the baseline? Does the project improve the protection of the Columbia River now or in the future? Are there measurable parameters that would document performance? Are these included in the proposal?)

1. The project represents a significant improvement compared to the current baseline of MNA
2. The project attempts to protect the Columbia River in the near term; however, the technology will not be ready for full-scale implementation for a number of years.
3. Performance of the technology will be measured by the current monitoring system, which must include monitoring throughout the plume in addition to the river's edge. Can other components besides uranium, e.g., sodium and phosphate, be monitored?

Summary Evaluation:
Overall, recommend this technology be implemented only if the project can address the issues described above. This will require a larger budget and more time. Consider combining this project with the apatite in 100-N Area and perform the tests in the laboratory side by side for both uranium and strontium. There may be some economy of scale with this approach, leaving some funding to address delivery and scaling, which are issues for all of the insitu remediation projects. Thumbs up with some minor suggestions.

Reviewer #5

Target Plume/Area: 300 Area

Proposal Title: 300 Area Uranium Plume Treatability Demonstration Project: Uranium Stabilization Through Polyphosphate Injection

Technical Basis of the Proposal:
Is the project or activity based on appropriate and valid science?
Yes. Project employs sound and novel techniques for time-release of phosphate for control of uranium source zone. Further, it employs a well-structured methodology to combine both laboratory analyses and pilot field study (and tie-in with ongoing site characterization study).

What is the technical likelihood of the stated-desired outcome?
Good, with concerns remaining regarding targeted injection considering heterogeneity of subsurface; longevity of autunite given conditions at site (including high phosphate concentrations); longevity of apatite sequestration mechanism, and need for long term monitoring of uranium plume.

How does the project fit in with the totality of proposed activities for the target contaminant/plume?
Previous efforts focused on source removal involving excavation, characterization, backfill, and surface restoration of the 300 Area liquid waste disposal sites. A Phase III Feasibility Study was begun in 2005 to identify and evaluate remedial alternatives that will accelerate monitored natural attenuation of the uranium plume. Polyphosphate application is judged to be the most promising among five other active remedial technologies for uranium at this site. Presently focused application of polyphosphate is proposed in source or "hot spot" areas that would significantly reduce the inventory of available uranium that contributes to the groundwater plume

Is the proposed approach reasonable and practicable?
Yes.

What are the risks or key uncertainties in the proposed action(s)?
Risks/uncertainties include: (i) method of injection and influence of heterogeneity; (ii) long-term sequestration effectiveness, to include stability of uranyl phosphate, apatite crystal size, long-term substitution, and long-term monitoring issues.

Are there clear examples of alternative ideas or proposals that should be considered?
No.

Implementation Strategy:
Is the sequence and timing of activities appropriate?
Yes.

Can the technology be implemented cost-effectively?
Likely.

Is the budget and level of effort appropriate for the proposed work?
Yes.

Proposed Performance Metrics:
Does the proposed project or activity represent a significant improvement compared to the baseline?
Yes, to some degree. Current baseline technology is focused on source removal; specifically, remediation of principal 300 Area liquid waste disposal sites by excavation, characterization, backfill, and surface restoration.

Does the project improve the protection of the Columbia River now or in the future? Yes. Where applied, the polyphosphate will reduce the overall risk from the groundwater by stabilizing the uranium within the aquifer matrix underground, under the 300 Area. This stabilization will eliminate/reduce the uranium concentrations from the water that is seeping out in springs in the riparian zone along the Columbia River bank. Basically it will reduce/eliminate this exposure pathway.

Are there measurable parameters that would document performance?
Yes. Hydraulic tests will be conducted following emplacement of the treatment zone and compared with pre-treatments values to assess the impact of treatment on aquifer hydraulic properties. Specifically, pre- and post-treatment hydraulic responses will be compared to determine whether any degree of aquifer plugging occurred. In addition, coring should be considered to ensure available uranium is indeed sequestered within autunite in the oxidized form, U^{6+}.

Are these included in the proposal?
Yes.

Summary Evaluation:
Good proposal. Strengths oriented towards time release capability of polyphosphate and tie-in with "limited" field tests. Concerns include (i) method of injection and influence of heterogeneity; (ii) long-term sequestration effectiveness, to include stability of uranyl phosphate, apatite crystal size, long-term substitution, and long-term monitoring issues. Considerations: addition of coring activity to field test evaluation to confirm sequestration state of uranium.

Reviewer #6

Target Plume/Area: U / 300 Area

Proposal Title: U Stabilization through polyphosphate injection

Technical Basis of the Proposal:
General

-- This project is generally consistent with previous peer reviews and recommendations.

-- this project in interesting and well conceived. The hydrolysis reaction that releases the phosphate is reliable and predictable (under a variety of conditions) and phosphate minerals of U are well studied and very stable. Phosphate based stabilization has been somewhat under-represented in the DOE research portfolio (relative to redox stabilization and biological reduction). This appears to be an appropriate alternative and may form immobilized phases that have more long term stability than reduced U minerals which are being observed to reoxidize at varying rates in both lab and field situations.

-- The objectives are clear and practical and well stated.

-- This technology does not require microbes, but what is the impact of microbes in the real world. Are there competing reactions for the phosphate that will make the process less efficient?

-- Heterogeneity will be important – what are advantages and disadvantages of each.

-- Salting out may be an issue in terms of sorption.

-- Is there any potential for a push-pull field test of some of the processes and rates? Similarly, would a dipole injection extraction deployment option mitigate the potential for spreading contaminated water?

-- Is there potential to use a mixture of polymer lengths to spread out the release over space and time?

-- EM has funded some tests of lactate (e.g., HRC) for chemical reduction based stabilization of metals with work on the Hanford site. This is a potential alternative that should be acknowledged – I favor the phosphate precipitation as proposed.

Implementation Strategy:
Schedule is generally reasonable.

Proposed Performance Metrics:
Reasonable performance metrics.

Summary Evaluation:
Good proposal. Need to address some of the specific uncertainties.

Reviewer #7

Target Plume/Area: 300-FF-5 Operable Unit, Hanford, WA

Proposal Title: 300 Area Uranium Plume Treatability Demonstration Project: Uranium Stabilization through Polyphosphate Injection

Technical Basis of the Proposal:

Is the project or activity based on appropriate and valid science? The science on which this proposal is based is the sequestration of uranium via the *insitu* precipitation of uranium minerals and the formation of apatite for uranium sorption. Many of the current technologies for uranium treatment rely on uranium reduction and sequestration as a U(IV) bearing mineral. This technology would not require uranium reduction, and therefore if it can be deployed successfully would overcome the potential problem of uranium re-oxidation and release from uraninite under oxidizing condition. The science appears to be valid, and if successful, could provide a new and valuable remedial tool.

What is the technical likelihood of the stated-desired outcome? From the supporting literature, it would seem that the technology can achieve the sated outcomes and the tasks set forth in the proposal should provide data to evaluate the efficacy of the technology.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? Baseline has focused on source removal and monitored natural attenuation. It is evident that natural attenuation will not be protective of the river as a sole strategy. The addition of phosphate to precipitate uranium minerals and produce apatite to further sorb uranium fits well with the current strategy and offers the potential to greatly accelerate reaching site goals.

Is the proposed approach reasonable and practicable? Yes.

What are the risks or key uncertainties in the proposed action(s)? The technology calls for the addition of polyphosphate to the subsurface that will hydrolyze allowing for free phosphate to precipitate meta-autunite and apatite. Key risks and uncertainties include the impact of adding large amounts of phosphate to the subsurface and potential changes in hydraulic parameters. However, the proposal outlines a rigorous analytical program that should help to quantify and/or predict the possible affects polyphosphate addition will have.

Are there clear examples of alternative ideas or proposals that should be considered? There are other possible actions that could also be tried, such as, traditional pump & treat or *insitu* reductive technologies. However, the proposed technology could offer some significant advantages over these other options and this reviewer believes that it is very worthwhile to evaluate this technology.

Implementation Strategy:
Is the sequence and timing of activities appropriate? Yes, large scale flow cell columns to precede scale-up to field scale pilot testing.

Can the technology be implemented cost-effectively? If proven to be effective and able provide a stable, long-term reservoir for uranium, this could be a cost-effective solution.

Is the budget and level of effort appropriate for the proposed work? Budgetary analysis is better addressed by those familiar with costs typically associate with this type of work at national labs.

Proposed Performance Metrics:
Does the proposed project or activity represent a significant improvement compared to the baseline? Yes. The natural attenuation and long-term ground water monitoring approach is not currently protective of the river, and therefore additional remedies appear to be required. The technology to be evaluated under this proposal could offer a significant improvement compared to baseline.

Does the project improve the protection of the Columbia River now or in the future? Yes.

Are there measurable parameters that would document performance? Yes.

Are these included in the proposal? Yes.

Summary Evaluation:
The primary objective of the work proposed here is to evaluate a technology that offers the potential to sequester uranium *insitu* via the precipitation of meta-autunite and adsorption onto apatite. If successful this could offer a powerful new remedial approach for uranium contaminated sites. The proposal provides for a combination of laboratory and field investigations that should provide the data required to evaluate the likelihood of successful deployment.

APPENDIX K

Carbon Tetrachloride and Chloroform Attenuation Parameter Studies:
Heterogeneous Hydrolytic Reactions

Target Plume/Area: Carbon Tetrachloride / Hanford 200 West Area, ZP-1

Proposal Title: Carbon Tetrachloride and Chloroform Attenuation Parameter Studies: Heterogeneous Hydrolytic Reactions

Reviewers: Brian Looney, Todd Anderson, Jackson Ellington, Jess Everett, Dawn Kabak, Gene Leboeuf, Joe Rossabi

Summary Evaluation:
The panel supports the proposed study. There was general consensus the proposal is based on appropriate and valid science and has merit to address the carbon tetrachloride (CT) plume. Moreover, the study would fill an existing science gap at Hanford and complements and leverages the current homogenous hydrolysis study. For a large plume like CT at Hanford, hydrolysis and similar degradation processes that are traditionally neglected may be significant in limiting contaminant migration.

Reductive processes that dominate attenuation at many sites are not operative at Hanford due the presence of oxygen and nitrate in the groundwater. In this case, hydrolysis rates of the chloromethanes, while slow, are likely to be a primary determinant in the potential for Columbia River impacts. The current remediation technology is soil vapor extraction and limited groundwater pump and treat. The proposed research is a key step in developing an overarching and long-term plan for CT and related contaminants at Hanford. Some technical issues/recommendations were identified by the panel, which should be considered by the investigators and DOE as the research plan is finalized and the work implemented. These concerns were primarily associated with the type(s) of solids used in the heterogeneous studies, the timing and sensitivity of the analysis, the total length of time needed for the study, the QA and equivalency requirements associated with a multi year study, etc.

Technical Basis of the Proposal:
In general, the panel believes the proposal is based on appropriate and valid science. The panel provided some specific technical issues for consideration. These are summarized below along with an identification of reviewers who provided detailed topical comments and recommendations. The researchers are strongly encouraged to read the relevant individual reviews as they finalize their plans.

- Consider clarifying the linkage with historical and ongoing work – expanding the discussion of how this study builds on the previous study of the homogeneous hydrolysis of chloroform (CF). (Reviewers 2, 6 and 7)

- Consider using real samples for heterogeneous experiments, including both sediments and groundwater. Existing sediment cores from the field should be used as the basis for selecting the minerals to use in the heterogeneous hydrolysis tasks. The basis for the selected solid materials to be tested needs to be carefully thought out and documented. The selection criteria for the sediments and brief justification should be provided to DOE. (Reviewers 1, 2, 3, 6 and 7)

- Sediment and groundwater samples need to be identified by their composition and where they were obtained. Consideration should be given to concerns regarding whether real sediment and groundwater samples can be considered representative of Hanford. (All Reviewers)

- Since a significant hydrolysis reaction could occur at ambient temperature, the proposal should consider inclusion of (or shifting to) a test point of 15 degrees centigrade, which is closer to the ambient temperature. (Reviewers 1,5 and 6)

- Address mineralogy concerns:
  - Milling and grinding sediments could produce reactive mineral states and influence test results. If the reactive minerals are coated on the sediment particles than typical assumptions and interpretation associated with ground sediment might underestimate attenuation – if the grinding exposed active reaction sites than the interpretation might overestimate attenuation. (Reviewers 1, 4, 5 and 6)
  - Consider conducting some bulk analysis of the raw sediment (looking for mineralogical distribution, coatings, etc.) as an adjunct to the microcosms. (Reviewers 1 and 6)
  - Identify the mineral powders that will be used in the study. The identification should be based on a clearly stated conceptual model and test specific hypotheses that will be used when modeling plume migration and stabilization. (All Reviewers)
  - Avoid using the terms “minerals” and “sediments” interchangeably. (Reviewer 1)

- Consider possible impacts of other contaminants in the CT plume, resulting from the original waste being a diverse mixture containing inorganic brine, and organic co-contaminants. (Reviewers 6 and 7)

- Identify and consider all daughter products that may have been produced by the contamination plume. The presence of daughter products may offset the positive effects of reducing the CT. (Reviewers 3 and 6)

Implementation Strategy:

- The proposed study complements an ongoing study, and is integrated well with current modeling work.

- Proposal appears to be cost-effective.

- Address concerns about the longevity of the proposed study:
  - The study will likely take between four to six years to complete. Funding through this program is only provided for two years, so subsequent funding will need to be secured to complete the study. Additional funding may be available, but some tangible progress must be demonstrated after two years.
  - Given the slow reaction rates at the lower temperatures to be used in the proposed study, determine whether useful data can be obtained within the proposed time frame. (All reviewers)

- In a multiyear study, issues of detection limits and quality assurance are of paramount importance. These issues should be carefully considered to assure proper sensitivity and detectability as well as to assure that data are usable. (see performance metrics)

Proposed Performance Metrics:

- In general, the performance metrics discussed in the proposal seem reasonable and appropriate. The hydrolysis parameters and the 95% confidence interval at 15 degrees centigrade are measurable parameters that will document performance.

- Support using perchloroethene (PCE) as an internal standard to monitor a possible decrease in CF and CT starting concentrations in water over five years. Assuming the same instrument and detector are used for the duration of the study, quality assurance was not described that would identify selective changes in detector response of CF, CT, or PCE. Based on the trend of the change in response, decreases in concentration of CT and CF could be calculated when in fact the concentrations had not changed. To monitor consistency of detector response, a sufficient supply of check samples to contain PCE and either CF or CT should be prepared in glass sealed tubes and stored refrigerated in the dark. The check samples should be analyzed as samples at each sampling period and the calculated concentrations of CT and CF should remain constant over the five years. Need to calculate detection limits to assure proper sensitivity to accurately measure expected changes. (All reviewers)

- Consider indicating how the disappearance of the contaminants will be monitored after two to five years.

Reviewer #1

Target Plume/Area: Hanford 200 West Area, ZP-1

Proposal Title: Carbon Tetrachloride and Chloroform Attenuation Parameter Studies: Heterogeneous Hydrolytic Reactions

Technical Basis of the Proposal:

Is the project or activity based on appropriate and valid science?

Yes. The proposed project is based on reasonable science. The PIs propose to investigate potential abiotic mechanisms of CT and CF degradation under conditions that approximate those found within the CT plume under the Hanford 200 West area. Of particular importance are the heterogeneous reactions catalyzed/aided by the interaction of CT and CF with potential minerals likely to be found in the Hanford subsurface. This is of importance because contaminants in groundwater are in contact with numerous mineral surfaces many of which may be reactive.

What is the technical likelihood of the stated-desired outcome?

The outcome of the proposed studies should be a better understanding of the interaction of CT and CF with potentially reactive subsurface minerals. This is of importance for projecting the mobility and natural attenuation of CT and CF within the subsurface.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable?

Given the enormous size of the CT plume (10km^2) and the depths both above and below the water table where CT contamination is found, MNA is likely to be the dominant remediation mechanism for this site. This project supports an MNA approach to CT remediation by evaluating potential abiotic mechanisms of degradation. Projected rates of degradation can then be incorporated into models of groundwater transport to make future projections of CT and CF movement and attenuation in the subsurface.

What are the risks or key uncertainties in the proposed action(s)?

The degradation experiments are to be conducted over a range of temperatures, none of which approximates the insitu temperature of the aquifer. Why not include at least one experiment at the insitu temperature (~15C)? Perhaps no degradation will be observed over the life of the experiment at this temperature but it is still worth doing. The risk of using observations at elevated temperatures to extrapolate rates of hydrolysis/reaction is that the extrapolated rates do not accurately represent the true rates of degradation.

Also, there is a potential to overestimate the rates of heterogeneous degradation of CT and CF via the proposed grinding procedure to be used on minerals obtained from the Hanford subsurface. Grinding can induce the formation of highly reactive species (such as Si radicals) in geomaterials that could interact with CT and CF and produce erroneously high rates of CT/CF degradation. Perhaps including an experimental suite that uses unground material from the sites should be included in the experimental design. After all, materials found in the subsurface are unground. What is the chosen set of minerals to be investigated? Quartz is likely to react differently than an Fe-oxide or reduced mineral (biotite).

Are there clear examples of alternative ideas or proposals that should be considered? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)
Various bioremediation options, ZVI treatments and bioaugmentation strategies are available to treat CT and CF plumes but, given the staggering size of the CT plume at Hanford, these technologies would probably only be appropriate for limited areas of high CT content. For much of the plume, natural attenuation mechanisms (abiotic mechanisms) are likely to dominate the degradation of CT and CF.

Implementation Strategy:
(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)
The proposed project is largely a laboratory study to be conducted over 3+ years. The budget appears appropriate for the work proposed.

Proposed Performance Metrics:
(Does the proposed project or activity represent a significant improvement compared to the baseline? Does the project improve the protection of the Columbia River now or in the future? Are there measurable parameters that would document performance? Are these included in the proposal?)
The proposed work is a complimentary project to an existing project looking at the homogenous hydrolysis of CT. The proposed investigations will extend evaluations of abiotic CT degradation to heterogeneous systems comprised of various minerals found in the subsurface at the Hanford site. The identity of the minerals to be investigated was not described. The work will also examine potential abiotic mechanisms of CF (a CT degradation product) degradation in the presence (and absence) of subsurface materials.
Once the experiments are done and the kinetics of degradation incorporated into models of contaminant transport, there was no indication on how model projections would be verified in the field, i.e. there is no discussion of performance metrics for use in the field.

Summary Evaluation:
This is a laboratory-based project to evaluate the abiotic mechanisms of CT and CF degradation under homogeneous (CF) and heterogeneous (CF and CT) conditions. I find this project to be of relevance to EM but it is perhaps more of a research project than applied science. It is of interest to know how/if CT and CF react with water and/or different minerals common to the Hanford subsurface. However the planned experiments will be conducted at temperatures still largely above groundwater temperature and therefore the rates of reaction will be estimated via extrapolation. This may not be appropriate. Also, for the heterogeneous reaction experiments, the identity of the minerals to be examined was not provided. Different minerals can behave differently towards CT and CF degradation, particularly reduced minerals containing Fe(II).

Also, the project mentions grinding the minerals collected from the Hanford subsurface to be used in the experiments. Grinding these materials can be problematic because grinding can induce the formation of reactive surfaces and reactive species within geomaterials (such as Si radicals). The generation of reactive species may result in an over estimation of the degradation of CT and CF in these experiments. An experiment suite using unground Hanford materials may be required to control for this.

Overall, the experiments are complimentary to existing CT degradation studies. I find the project a reasonable approach to evaluating the abiotic mechanisms of CT and CF degradation but one that could be improved by including experiments at the insitu temperature and including unground Hanford materials in the experimental setup.

I recommend that this project go forward.

Reviewer #2

Target Plume/Area: Hanford 200 West Area, ZP-1

Proposal Title: Carbon Tetrachloride and Chloroform Attenuation Parameter Studies: Heterogeneous Hydrolytic Reactions

Technical Basis of the Proposal:
Research on the homogeneous hydrolysis of halogenated compounds started decades ago. The proposed homogeneous hydrolysis study of chloroform (CF) incorporates the historical knowledge for conducting elevated temperature studies into the experimental. The CF proposal also complements an ongoing project to determine the homogeneous hydrolysis of carbon tetrachloride (CT). The main goal of the CF hydrolysis study is to reduce the uncertainty of a hydrolysis rate extrapolated from higher temperatures to groundwater conditions. As such reaching the desired outcome is high.

Literature is sparse on the heterogeneous hydrolysis of halogenated chemicals under oxygenated conditions. CF concentrations were reported up to1, 100µg/L in one of the monitoring wells. The CF was most likely formed by subsurface degradation of CT, during an up to 30-year residence time, rather than during the industrial use of CT. The Hanford groundwater is reported to contain oxygen in the depths traversed by the CT plume, which would seem to indicate that CF was not formed under iron reducing conditions. However, could localized pockets of anoxic conditions exist in the Hanford groundwater that would support reductive degradation of CT? The heterogeneous hydrolysis studies with silt and clay in sterile Hanford groundwater are reasonable and practicable but even with temperatures up to 40 ^{o}C the study may not be of sufficient duration to obtain measurable degradation of CT. If no degradation is observed in the heterogeneous studies the source of CF in groundwater will remain unknown.

See Summary Evaluation for suggestions.

Implementation Strategy:
Is the sequence and timing of activities appropriate? Yes
Can the technology be implemented cost-effectively? Yes
Is the budget and level of effort appropriate for the proposed work? Yes

Proposed Performance Metrics:
Does the proposed project or activity represent a significant improvement compared to the baseline? Does the project improve the protection of the Columbia River now or in the future? Are there measurable parameters that would document performance? Possible decrease in CF and CT starting concentrations in water will be monitored over five years using perchloroethene (PCE) as an internal standard. Assuming the same instrument and detector are used for the duration of the study, quality assurance was not described that would identify selective changes in detector response of CF, CT, or PCE. Based on the trend of the change in response, decreases in concentration of CT and CF could be calculated when in fact the concentrations had not

changed. To monitor consistency of detector response, a sufficient supply of check samples to contain PCE and either CF or CT should be prepared in glass sealed tubes and stored refrigerated in the dark. The check samples should be analyzed as samples at each sampling period and the calculated concentrations of CT and CF should remain constant over the five years.
Are these included in the proposal? No.

Summary Evaluation:
The desorption studies reported in PNNL-15239, described the collection of intact sediment cores from a borehole 6 meters from the south boundary of the 216-Z-9 trench. The cores were used to determine Kds of CT and CF. The bulk physical and chemical characteristics of sediment cores were reported. In the groundwater collected at 292-294 meters the CF concentrations were 400 µg/L and CT 2463 µg/L. The % organic carbon increased with depth and was 0.088 in the 430-meter core. In the cores collected at 292 meters and below up to 70% by mass of CF remained bound to the sediment after the desorption experiments.

If any of the sediment cores remain, they would be a better choice to the heterogeneous hydrolysis study. Use of C-13 labeled CT and monitoring C-13 labeled products would allow monitoring degradation.

For Task 2 and Task 3 heterogeneous hydrolysis studies the only description of the silt and clay was: “The sediment will consist of uncontaminated silt and clay from the Lower Ringold formation near the 200 West area of the Hanford site.”

Were the sediments for the heterogeneous hydrolysis study collected to approximate the sediments used in the desorption studies?

Does the clay contain ferruginous smectite?
Ferruginous smectite from Grant County, Washington was shown to degrade pentachloroethane under reducing conditions (J. Cervini-Silva et al., Dechlorination of pentachloroethane by commercial Fe and ferruginous smectite” Chemosphere 47 (2002) 971-976).

Reductive dehalogenation by low concentrations of natural organic carbon was proposed and shown to be consistent with published literature by J. Washington “Hydrolysis Rates of Dissolved Volatile Organic Compounds: Principles, Temperature Effects and Literature Review”, 33 (1995) 415-424.

Reviewer #3

Target Plume/Area: Hanford 200 West Area, ZP-1

Proposal Title: Carbon Tetrachloride and Chloroform Attenuation Parameter Studies: Heterogeneous Hydrolytic Reactions

Technical Basis of the Proposal:

1. *Is the project or activity based on appropriate and valid science?* Previous studies indicate that porosity, sorption, and abiotic degradation greatly influence Carbon Tetrachloride (CT) plume behavior. Homogeneous hydrolysis reaction rates at high temperatures are available for CT and Chloroform (CF), but there is significant uncertainty when these results are used to estimate rates at normal groundwater temperatures. In turn, this creates large uncertainties when predicting natural attenuation of the CT plume found at the Hanford site. In fact, the range of abiotic degradation rates is so large that higher values result in significant attenuation while lower values result in insignificant attenuation of the CT plume. The Hanford Groundwater Project has recently initiated a study to determine the homogeneous hydrolysis rate of CT at temperatures closer to Hanford ambient groundwater temperatures. However, no information is available, or currently being collected, for the heterogeneous hydrolysis of CT at such temperatures. Furthermore, no information is available, or under collection, concerning the homogeneous or heterogeneous hydrolysis of CF at Hanford ambient groundwater temperatures. CF is an important CT degradation product. Specifically, the investigators will measure hydrolysis rates at temperatures from 20 to 70 degrees centigrade under homogeneous and heterogeneous conditions for CF and heterogeneous conditions for CT. Studies of heterogeneous reactions will incorporate natural sediment (uncontaminated silt and clay from the Lower Ringold formation near the 200 West Area of the Hanford Site) and mineral powders (four representative minerals ground to fine-silt size, chosen from appropriate clays, zeolites, feldspars, and iron oxides). CF, PCE, and possible organic degradation products will be measured from sacrificed Pyrex glass bulbs. Confidence intervals of the hydrolysis rate down to 15 degrees centigrade will be estimated from the data. The proposed study could greatly improve estimates of abiotic degradation resulting from hydrolysis and reduction reactions. This could greatly improve the prediction of natural attenuation at the site, critical for applying monitored natural attenuation (MNA) and determining if active remediation is needed. Thus, the project is based on appropriate and valid science.
2. *What is the technical likelihood of the stated-desired outcome*? The rate of hydrolysis decreases with decreasing temperature. The investigators state that useful results can be obtained within the funding period. But they also indicate that, to obtain the best possible data, they will extend the project beyond the current proposed time period. How important is this? How likely is it that that the required funds will be obtained to extend the experiment? Can the described experiments obtain useful results within the two-year time frame? What is the time frame of the Hanford Groundwater Project's homogenous hydrolysis study of CT at lower temperatures? Based on existing data, such as the possible range of hydrolysis rates and the minimum chemical concentration changes that can be detected given the experimental design and available analytical equipment, the investigators could provide a

more complete justification their statements regarding project duration. Otherwise, the technical likelihood of the stated-desired outcome is high.

3. *How does the project fit in with the totality of proposed activities for the target contaminant/plume*? Current remediation of the CT plume involves vapor extraction and Pump & Treat. According to the (draft) "Supplemental Activities to Protect the Columbia River Adjacent to the Department of Energy Hanford Site: Management Strategy and Implementation Status" report dated February 2006, for CT in the 200 areas (Attachment 3), proposed technologies include an attenuation parameter study and the installation of deep recovery wells. Regarding an attenuation parameter study, the report indicates that such a study is "the most relevant project related to the question of carbon tetrachloride migration to the Columbia River from the 200 Area." The report authors recommend funding an attenuation parameter study through the Congressional supplemental allocation. The proposal reviewed here will provide important attenuation parameters, required for any evaluation of monitored natural attenuation evaluation of the Area 200 CT plume. Thus, the project fits well within the totality of proposed activities for the target contaminant/plume.
4. *Is the proposed approach reasonable and practicable*? The proposed approach is reasonable and practicable. However, as stated previously (in #2, above), this reviewer would like to see an assessment of the range of experiment durations required to obtain estimated of the various hydrolysis rates. Additional issues are described in #5, below.
5. *What are the risks or key uncertainties in the proposed action(s)*? There are three key risks/uncertainties. First, given the slow reaction rates at the lower temperatures to be used in the proposed study, can useful data be obtained within the proposed time frame (as already discussed in #2, above)? Second, can the results for heterogeneous hydrolysis, based on studies with a single natural sediment from one location and four mineral powders, provide enough information for a natural attenuation study of the CT plume in Area 200 of the Hanford site? Will the chosen natural sediment be representative of the site? There appears to be some uncertainty regarding the location of the source of CT at the site, indicating there is also uncertainty regarding the location and extent of the plume. Can one natural sediment sample be used to represent sediments the plume will travel through, from source to the Columbia River? Or should multiple sediment samples, from various locations at the site be used? Similarly, the investigators have not indicated what mineral powders will be used. Is there sufficient information available from the site to select the appropriate mineral powders? Will the mineral powders be selected based on the single sediment sample the investigators currently intend to use, or will selection be based on the range of sediments the plume may encounter between Area 200 and the Columbia River? Third, it is important that all daughter products are identified, as the production of hazardous, recalcitrant daughter products may negate the positive effect associated with hydrolysis reducing the concentration of CT. Will sufficient effort be expended to identify and quantify daughter products?
6. *Are there clear examples of alternative ideas or proposals that should be considered*? The work described by the investigators is appropriate for

<u>If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations</u>) According to the (draft) "Supplemental Activities to Protect the Columbia River Adjacent to the Department

of Energy Hanford Site: Management Strategy and Implementation Status" report dated February 2006, this is not an expedited review.

Implementation Strategy:

1. *Is the sequence and timing of activities appropriate*? The sequence of events is appropriate. The two-year duration of the project may not be sufficient to provide adequate estimates of hydrolysis rates at lower temperatures; however, the authors intend to obtain funding to continue the study.
2. *Can the technology be implemented cost-effectively*? The proposed work provides parameters that would be used to estimate natural attenuation of the CT plume. This information would in turn be used to evaluate the appropriateness of Monitored Natural Attenuation (MNA) or some combination of MNA and active remediation. MNA is considered a cost-effective strategy.
3. *Is the budget and level of effort appropriate for the proposed work*? Yes.

Proposed Performance Metrics:

1. *Does the proposed project or activity represent a significant improvement compared to the baseline*? Yes, the currently available estimates of homogenous and heterogeneous hydrolysis rates for CF and heterogeneous hydrolysis rates for CT, at appropriate groundwater temperatures, have unacceptable uncertainty. The proposed work will provide much better estimates, which can be used to evaluate MNA or some combination of MNA and active remediation.
2. *Does the project improve the protection of the Columbia River now or in the future*? The project will help in the determination of the most cost-effective strategy regarding the CT Plume, thus, it will the protection of the Columbia River in the future.
3. *Are there measurable parameters that would document performance*? The hydrolysis parameters and the 95 % confidence interval at 15 degrees centigrade are measurable parameters that will document performance.
4. *Are these included in the proposal*? Yes.

Summary Evaluation:

The investigators will measure hydrolysis rates at temperatures from 20 to 70 degrees centigrade under homogeneous and heterogeneous conditions for CF and heterogeneous conditions for CT. Studies of heterogeneous reactions will incorporate natural sediment (uncontaminated silt and clay from the Lower Ringold formation near the 200 West Area of the Hanford Site) and mineral powders (four representative minerals ground to fine-silt size, chosen from appropriate clays, zeolites, feldspars, and iron oxides). CF, PCE, and possible organic degradation products will be measured from sacrificed Pyrex glass bulbs. Confidence intervals of the hydrolysis rate down to 15 degrees centigrade will be estimated from the data. The proposed study could greatly improve estimates of abiotic degradation resulting from hydrolysis and reduction reactions. This could greatly improve the prediction of natural attenuation at the site, critical for applying monitored natural attenuation (MNA) and determining if active remediation is needed.

There are three areas of concern related to the project. The concerns are listed in order of priority. First, given the slow reaction rates at the lower temperatures to be used in the proposed study, can useful data be obtained within the proposed time frame. Second, can the results for heterogeneous hydrolysis, based on studies with a single natural sediment from one location and four mineral powders, provide enough information for a natural attenuation study of the CT plume in Area 200 of the Hanford site? Third, will all daughter products be identified? The production of hazardous, recalcitrant daughter products may negate the positive effect associated with reducing the concentration of CT. Will sufficient effort be expended to identify and quantify daughter products? Optimization of the study requires addressing these concerns; however, let it be noted that even if all three concerns turn out to have some validity, the study can still provide useful information.

Reviewer #4

Target Plume/Area: Carbon Tetrachloride/ 200 West Area

Proposal Title: CT and Chloroform Attenuation Parameter Studies: Heterogeneous Hydrolytic Reactions

Technical Basis of the Proposal:
(Is the project or activity based on appropriate and valid science? What is the technical likelihood of the stated-desired outcome? How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable? What are the risks or key uncertainties in the proposed action(s)? Are there clear examples of alternative ideas or proposals that should be considered? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)

The proposal calls for laboratory testing of CT and chloroform (CF) hydrolytic reactions to contribute to the basis for predicting CT plume behavior in the 200 Area at the Hanford Site. Predictions for plume behavior are highly dependent upon porosity of the aquifer, sorption, and abiotic degradation. Little is known about abiotic degradation of CT and CF, especially at ambient temperatures. A study of homogeneous abiotic degradation of CT is currently underway. This proposal is based upon valid and appropriate science to enable improved predictions of plume behavior. The introduction of heterogeneous testing may improve the validity of the results. However, because little work has been done in this area, the limited tests proposed may not answer all questions.

There is some concern about the achieving the desired outcome, as the project would be funded for only two years and it is quite likely that more time would be required to collect applicable data. The reviewer is hopeful that DOE-RL would recognize the value of continuing the experiments for a much longer time.

The project is part of an overall plan to characterize the CT plume to enable improved decision-making regarding a remedial option, i.e. the Feasibility Study. Specific efforts, such as the DNAPL Conceptual Model Project and the homogeneous hydrolytic degradation experiments, have been employed to enhance plume understanding. This has been done in addition to significant efforts at characterization, as well as a pump and treat system and a soil vapor extraction system. A systems approach is definitely underway for this challenging problem.

The proposed approach is reasonable and practicable, but will likely have to be continued and possibly expanded after results of preliminary tests are obtained. The reviewer questions the use of Hanford groundwater and what that means. Will the groundwater be collected from a pristine area or will it be from a plume where there are high concentrations of co-contaminants, such as hundreds of parts per million of nitrate? There is also concern about using a single sediment sample to represent the entire stratigraphic section over the entire 200 Area of the site. In addition, there is concern about sample prep changing the reactivity of the mineral grains.

Perhaps they should consider using sediments from the Hanford formation rather than the Ringold, so that grinding doesn't have to be done. The reviewer suggests that additional testing will likely be necessary after preliminary results from this study are obtained using the simple tests proposed herein. The reviewer currently supports funding of this project, recognizing some limitations it may have.

The major risks are that the project will have to be extended over a longer period of time and additional test runs will have to be conducted to look at the variability of other parameters, such a mineralogy and groundwater chemistry.

Implementation Strategy:
(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work? <u>If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)</u>

There is no problem performing the laboratory tests. It is a relatively low-cost investment.

Proposed Performance Metrics:
(Does the proposed project or activity represent a significant improvement compared to the baseline? Does the project improve the protection of the Columbia River now or in the future? Are there measurable parameters that would document performance? Are these included in the proposal?)

This project, if successful, could improve the protection of the Columbia River, in the future. Measurable parameters for this project will be the analytical data obtained demonstrating the abiotic degradation rates for both CT and CF.

Summary Evaluation:
The proposal calls for laboratory testing of abiotic degradation rates for CT and CF to enable better predictions of the CT plume, as related to natural attenuation, in the future. The reviewer supports funding of this laboratory study, but cautions regarding the ability to have viable data within the project schedule and suggests that it is likely additional tests with other variables, such as groundwater chemistry and mineralogy, may be required. The impact of hydrolysis will likely not be significant to the overall attenuation process, but this work can help reduce the uncertainty associated with the analysis. Issues related to temperatures, concentrations, and sample preparation need to be considered prior to selection of final parameters.

Reviewer #5

Target Plume /Area: Carbon Tetrachloride / Hanford 200 Area

Proposal Title: Carbon Tetrachloride and Chloroform Attenuation Parameter Studies: Heterogeneous Hydrolytic Reactions.

Technical Basis of the Proposal:
Is the project or activity based on appropriate and valid science?
Yes. The sheer magnitude of the carbon tetrachloride (CT) plume in the 200 Area of the Hanford site suggests that natural attenuation processes will be an extremely important part of the overall strategy to reduce, contain, and control the CT plume. Because biodegradation is not considered a significant factor in degradation of CT at the 200 Area, improved understanding of abiotic degradation processes is essential for determining the long-term fate and transport of CT. Objectives of this work expand on the ongoing FY 2006 work to quantify homogeneous hydrolysis rates for CT under near-ambient temperatures by investigating impact and mechanisms of representative Hanford mineral services on hydrolysis rates for CT, and homogeneous and heterogeneous hydrolysis rates for chloroform (CF). Quantification of hydrolysis rates of CT is an important research need as previous works in this area possess significant uncertainties in parameter values when the results are extrapolated to ambient temperatures relevant to the subsurface at Hanford (~15^{o}C)

What is the technical likelihood of the stated-desired outcome? Very good. The research team is well established in this field, and has published numerous technical reports and archival journal papers on related topics. Further, the work is supported by previous Monte Carlo simulations of 1D transport models and 3D deterministic studies that suggest that existing hydrolysis data span such a range that there is significant uncertainty if the CT plume would be attenuated (some results suggest that it will, other results suggest the opposite). Additional strengths include the fairly robust nature of the proposed tasks, incorporating a fairly large number of experimental units overall. Unfortunately, the proposal lacks sufficient detail in a few areas, raising the following concerns: (i) the proposed temperature range for study is 20^{o}C through 70^{o}C – hwy not explore the most appropriate temperature for this study, 15^{o}C, as the lower temperature bound; thereby avoiding over-extrapolation of model fits to the data; (ii) are the analytical methods of mass spectrometry or electron capture detector sensitive enough to capture the potentially small differences in CF, PCE, and other organic degradation products given the relatively small rates of reaction expected in this work? (perhaps the quality control/quality assurance portion of the analytical methods can be expanded to show how such small changes in concentration can be differentiated); (iii) use of "mineral powders" as described in Task 2 are not defined – what minerals are proposed for use, and how do these minerals relate to the site conditions at Hanford?; (iv) Hanford sediments, as noted in the proposal for heterogeneous hydrolysis experiments, is also not well defined (i.e., how representative are these sediments relative to the range of sediments within the CT plumes; (v) what confidence level exists in the sorption coefficients for CT and CF in 200 Area sediments, and how do ranges/distributions of these model parameters influence the fate and transport of CT and CF? (related question: are they modeled as linear or nonlinear processes, and what is the impact on plume behavior using a linear or nonlinear sorption model?); and (v) the proposal represents 2 years of effort, yet some results, especially at the lower temperatures, may not yield sufficient information during this time period to provide the goal reduction in hydrolysis rate uncertainty; further, the proposal notes that longer-term work, if warranted, would be funded separately – through what methods will funding be obtained? Suggest that the proposal expand its scope to include funding for analysis of sample results for longer terms, especially in the case of the lower temperatures.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? This effort represents a very important component of the overall effort to quantify and understand environmental influences upon hydrolysis rates for CT and CF. While fundamental in nature, the overall results will be very important in the decision-making process for determination of what other active remediation technologies, if any, should be employed to effectively contain the CT plume.

Is the proposed approach reasonable and practicable?
Yes. The approach is reasonable and practicable, subject to the aforementioned concerns.

What are the risks or key uncertainties in the proposed action(s)?
Risks/uncertainties include: (i) ability to effectively capture very small changes in degradation products over extended time frames (years) with confidence that observed behaviors can indeed be solely attributed to hydrolysis reactions; (ii) site heterogeneity causing difficulty representing well the range of Hanford sediment materials expected within the range of the CT plume; and (iii) ability to conduct (or fund) longer-term experiments under lower temperature conditions most relevant for the conditions at the Hanford site.

Are there clear examples of alternative ideas or proposals that should be considered?
Yes. Employment of longer-term experiments and at the lower temperature bound of 15^{o}C.

Implementation Strategy:
Is the sequence and timing of activities appropriate?
Yes.

Can the technology be implemented cost-effectively?
Yes. Proposed work consists of lab-scale experiments to better understand the mechanisms for hydrolysis of CT and CF under a variety of environmental conditions.

Is the budget and level of effort appropriate for the proposed work?
Yes, the budget is fair and reasonable for the proposed two-year effort.
Proposed Performance Metrics:
Does the proposed project or activity represent a significant improvement compared to the baseline?

Potentially – if the experimental temperatures address 15°C, and the timeline of the experiments are expanded beyond two years. Otherwise, it is likely that the information obtained from this study will be insufficient to improve the uncertainty regarding hydrolysis rates of CT and CF.

Does the project improve the protection of the Columbia River now or in the future?
Yes, albeit a longer-term effort. Nonetheless, results of this study may provides sufficient data to reduce the uncertainly regarding the fate and transport of the CT plume, and to assist in determining to what extent active remediation needs to be applied to the plume.

Are there measurable parameters that would document performance?
Yes. This effort, with modification, will result in the production of hydrolysis rate data for CT and CF under a variety of environmental conditions.

Are these included in the proposal?
Yes.

Summary Evaluation:
A well-written, well-motivated proposal that can potentially provide very valuable insights to hydrolysis rates of CT and CF under a variety of environmental conditions. Strengths of this proposal include (i) use of an experienced and highly qualified team; and (ii) use of well-controlled laboratory-scale experiments to determine hydrolysis rates; (iii) use of three pH values for examination of homogeneous and mineral-surface catalyzed hydrolysis reactions for CF; and (iv) use of Hanford site minerals to begin to evaluate the impact of mineral surface chemistry on observed reactions rates. Concerns include: (i) need to use 15°C as the lower temperature bound to avoid over-extrapolation of model fits to the data; (ii) quality control/quality assurance of analytical methods over extended time periods; (iii) use of unidentified "mineral powders" as described in Task 2; (iv) Hanford sediments, as noted in the proposal for heterogeneous hydrolysis experiments, is also not well defined (i.e., how representative are these sediments relative to the range of sediments within the CT plumes; (v) influence of ranges/distributions of sorption model parameters on the fate and transport of CT and CF?; and (v) difficulty in obtaining sufficient information in the proposed 2 year time frame provide the goal reduction in hydrolysis rate uncertainty. *Recommend funding subject to addressing of aforementioned concerns.*

Reviewer #6

Target Plume/Area: Carbon Tetrachloride / 200 Areas

Proposal Title: Carbon Tetrachloride and Chloroform Attenuation Parameter Studies: Heterogeneous Hydrolytic Reactions

Technical Basis of the Proposal:

While the carbon tetrachloride (CT) plume is currently not entering the Columbia River, the "footprint" is large. Due to limited vertical concentration data throughout the aquifer, heterogeneity, changing boundary conditions such as falling water tables, difficulty and expense of monitoring, and other factors, the current extent and future migration of the CT plume is subject to significant uncertainty. Note that the term CT plume is often used as shorthand to describe the target problem, but the original waste was a diverse mixture containing inorganic brine, and organic co-contaminants. Large volumes of water were disposed in the vicinity of the release providing a driving force for penetration of the waste components. Once in the subsurface, this plume was subject to transport and partitioning processes. CT and other organic compounds in the waste are subject to degradation and generation of breakdown products. Previous modeling indicates that the rate of CT hydrolysis has a controlling impact on plume growth, stabilization and/or discharge. Further, the estimated range of hydrolysis rates used in the projections is based on a few studies performed under a limited set of conditions. Thus, improvement of the hydrolysis rate estimates and reduction in the uncertainty in this parameter will directly improve the understanding of and management of Hanford contaminants that might impact the Columbia River – the work directly addresses the Congressional mandate.

A FY2006 research study is underway improve estimates of hydrolysis rates at temperatures relevant to Hanford groundwater by performing experiments at lower temperature (thus reducing the need for "Arrhenius" projections far from the experimental conditions). The research proposed in response to the Congressional Mandate sets important additional objectives including: 1) study of chloroform (CF, a prominent co-contaminant), 1a) examination of expanded conditions for homogeneous hydrolysis (to account for potential base catalyzed CF reactions), and 2&3) study of heterogeneous hydrolysis to determine if mineral phases are participating in any abiotic hydrolysis or degradation reactions (this will be performed for both CT and CF)..

The current remediation technology is soil vapor extraction and limited groundwater pump and treat. The proposed research is a key step in developing an overarching and long-term plan for CT and related contaminants at Hanford.

Task 1 experimental protocol is generally well conceived (e.g., use of PCE as an internal standard, replicates, etc.). The experiments may extend beyond the 18-month time frame, but preliminary results should be available and the costs beyond that point should be relatively low (compared to the initial set-up).

Task 2 experimental protocol is reasonable. It is not clear why Ringold sediments were selected (versus Hanford Formation) but it may be that the investigators are working from the conceptual model that the long transport to the river would be via the Ringold Formation (especially after water levels re-equilibrate at lower elevation without Hanford operations and water discharges). The selection criteria for the sediments and brief justification should be provided to DOE. Similarly, the impact of milling and grinding is potentially problematic. If the reactive minerals are coated on the sediment particles than typical assumptions and interpretation associated with ground sediment might be conservative – if the grinding exposed active reaction sites than the interpretation would be optimistic. Some additional bulk analysis associated with the raw sediment (looking for mineralogical distribution, coatings, etc.) might be a useful adjunct to the microcosms. The experiments are proposed for sterile groundwater – are the sediments also sterilized.

Task 3 – see above (Task 2).

Implementation Strategy:
The lab research proposed has significant potential to reach the stated objective, some of the tasks may require extension beyond the circa two year time associated with the this program.

Proposed Performance Metrics:
Reasonable – the accuracy and precision of the work is tied to the information needed to understand and manage the CT plume to protect the Columbia River.

Summary Evaluation:
This proposal is appropriate and provides and key information to determine how the carbon tetrachloride plume might impact the Columbia River. Because the contaminated aquifers contain significant levels of electron acceptors (e.g., dissolved oxygen and high levels of co-disposed nitrate) biological reductive attenuation processes are improbable. Aqueous and heterogeneous hydrolysis, while relatively slow, may be important for large sites and plumes such as the 200 area at Hanford. The proposed tasks were generally logical and supportive of the objectives. A few technical issues/suggestions were identified in the review. These should be considered by the investigators and DOE as the research plan is finalized and the work implemented.

Reviewer #7

Target Plume/Area: Hanford 200 West Area, ZP-1

Proposal Title: Carbon Tetrachloride and Chloroform Attenuation Parameter Studies: Heterogeneous Hydrolytic Reactions

Technical Basis of the Proposal:
The goal of this proposal is to fill in gaps of understanding concerning natural reactions occurring that have and/or are remediating chlorinated contaminants in the soil and groundwater in the 200 West Area subsurface. Specifically, the researchers want to narrow the uncertainty of CCl4 and CHCl3 hydrolysis rates. The examination of hydrolysis rates in conditions that approximate the Hanford subsurface is an appropriate and valid pursuit. The experiments and parameters described are likely to provide better estimates of hydrolysis rates than are in the current literature. The results from this project should help to reduce the uncertainty of the residual contaminant inventory, bound contaminant reduction rate, and may provide parameters for potential intervention to accelerate contaminant remediation. The proposed approach is generally reasonable. Because of the relatively slow hydrolysis kinetics (in the 3 year time frame specified by funding cycle) anticipated, higher than ambient temperatures and higher than currently found concentrations will be used in the experiments to facilitate more accurate rate measurements. The extrapolation of rates to ambient conditions will force uncertainty. Additional uncertainty is added by the representative-ness of the abstracted sediments and their condition ex situ. This uncertainty is difficult to avoid. Although there are probably other ways of acquiring the desired results, the methods proposed here are consistent with current practice from the literature.

Implementation Strategy:
Sequence and timing appear to be appropriate. This proposal leverages other funded work with regard to technique and equipment. The budget appears to be consistent with many other DOE research projects. There may be some budget impact if the project length is extended to better capture the slower hydrolysis rates at ambient temperatures and lower concentrations.

Proposed Performance Metrics:
If successful, this project may provide an important improvement to the understanding of the fate of CHCl3 and CCl4 in Hanford sediments. In addition to determining the significance of hydrolysis as a natural degradation mechanism, it may provide insight into the viability of intervention to enhance hydrolytic processes. The current research on CCl4 hydrolysis was generally conducted at higher temperatures and in homogeneous solutions and may be missing important components affecting rates. The proposed experiments complement the current literature and provide a small amount of overlap for comparison.

Summary Evaluation:

Overall, I recommend funding this project for several reasons:

1. The results may help refine contaminant inventory estimates and decrease the uncertainty in the prediction of the contaminants persistence in the subsurface. This will help in the selection of appropriate strategies for the protection of the Columbia River.
2. It complements and leverages current CCl_4 hydrolysis experiments and equipment.
3. It may provide insight into the viability of manipulating conditions to enhance hydrolytic rates
4. It fills an important gap in the literature with respect to natural degradation mechanisms.

There are a few issues that need to be more fully addressed before funding including:

1. Likely typographical error on the test contaminant initial concentrations – should not be 100 and 1000 ppm (mg/l) – more likely meant 10 and 100 or 40 and 400 mg/l. In any case, lower concentrations (closer to ambient conditions at 200 west) should be used. The concentrations should be as close to ambient concentrations as possible without sacrificing definitive determination of the contribution of hydrolysis (i.e., there should be enough concentration signal above the noise to definitively determine the effect of hydrolysis).
2. Lowest experiment temperature should be approximately ambient subsurface temperature despite the likelihood that data may be too noisy at that temperature. Again there is a tradeoff between signal to noise and conditions approaching those occurring in the subsurface at 200 west. Additional budget may be necessary for additional controlled temperature apparatus beyond equipment that was being leveraged from current CCl_4 experiments.
3. Budget should be provided for additional experimental equipment and preparation costs for longer term studies.
4. In heterogeneous (soil/water) experiments, more detail should be provided with respect to measuring a mass balance, e.g., sorbed chemicals on sediment and containers should be extracted and measured.

APPENDIX L

Deep Carbon Tetrachloride (CT) Contaminant Assessment in the Vicinity of 216-Z-9

Target Plume/Area: Hanford 200-West Area in the vicinity of 216-Z-9

Proposal Title: Deep Carbon Tetrachloride (CT) Contaminant Assessment in the Vicinity of 216-Z-9

Reviewers: Dawn Kaback, Todd Anderson, Jess Everett, Gene Leboeuf, Ralph Nichols

Summary Evaluation:

The panel believes the proposal provides a creative approach for using existing infrastructure and a proven technology, aquifer testing, to assess CT contamination as dense non-aqueous phase liquid (DNAPL) in the unconfined aquifer beneath a known source zone, the 216-Z-9 Trench in the 200 West Area of the Hanford site. However, the panel has significant concerns about the ability of the proposed pumping test results to definitively demonstrate the presence or absence of DNAPL at this specific location. The proposal provides too little information to the panel to adequately assess whether the pumping test is appropriately designed to attain the desired results (e.g., lack of information on conceptual model, geology, well locations and screen intervals, modeling to support design of the pumping test) and given our knowledge of the Hanford subsurface, we recognize the significant uncertainties associated with interpretation of the results of such a test, as it is currently designed. Based upon the proposal we reviewed, the review team does not believe sufficient detailed work has been demonstrated on the conceptual model of DNAPL potentially trapped in the unconfined aquifer and on the three-dimensional flow field to be induced during the pumping test.

The panel recommends the project be conducted through two phases with a go/no go decision made after completion of Phase One. Phase Two will consist of the actual pumping test. Phase One consists of three activities: 1) demonstration of the location of a potential DNAPL trap through validation of the conceptual model with surface or cross-borehole geophysics (new or existing data); 2) additional numerical modeling to determine the viability of the test to attain the objective of demonstrating the presence or absence of DNAPL based upon the location of a potential DNAPL trap, selection of a pumping well, and design of the pumping test (Reviewers #1, 2, and 3); and 3) evaluation of three confidence intervals related to the measured CT concentration in terms of possibility of DNAPL presence or absence.

The panel recommends that the additional numerical modeling involve stochastic methods and particle tracking to demonstrate capture of the plume at the targeted volume both horizontally and vertically within the aquifer and to define optimum parameters, such as pumping rates and pumping time for design of the test (this should include determination of whether the shallow pumping well can perform the proposed effect; whether and how quickly DNAPL can be measured using the deep test well that has a fifty-foot screen installed (such a long screen may not provide optimum conditions for detecting DNAPL at the base of the aquifer).

In addition, the panel expressed significant concern regarding the use of a breakpoint, 8 mg/l, to indicate presence/absence of DNAPL. The panel recommends that the stochastic modeling define confidence intervals, which would include "DNAPL likely," "DNAPL unlikely," and "DNAPL possible." If the "DNAPL possible" range is extremely broad, the test would not be definitive and its value may be poor. The recommended modeling would enable prediction of specific confidence intervals, which would support the go/no go decision regarding the value of the test at the end of Phase One.

The panel also expressed concern as to how this test fits in with the conceptual model of DNAPL in this portion of the 200 West Area (Reviewer #2). Where does the conceptual model predict the location of the DNAPL? Is it immediately beneath the source area, such as the Z-9 Trench or has it migrated laterally due to flow along the top of the Ringold Mud to an area of low topography (i.e. a trap)? The panel recommends that a surface or cross-borehole geophysical survey (either existing or newly collected) be used to map the topography on the top of the Ringold Mud, prior to the design of the pumping test (this could alter the selection of the pumping well). What do the data recently collected from the cross-borehole seismic survey at the Z-9 Trench show in terms of topography on the top of the Ringold Mud? This work has already been completed and results should be utilized to reduce uncertainty for the proposed test. In addition, the work of Waddell might prove to provide some understanding of the potential location of the DNAPL trap. The fact that the proposed pumping test, as currently designed, only targets a small area as a proposed DNAPL trap should be explained to stakeholders before it is conducted.

The panel recommends conduct of the pumping test, only if the Phase I work shows an ability to reduce uncertainty so that the proposed test could meet its objectives.

Technical Basis of the Proposal:
The proposal describes the plan for conducting a pumping test to determine the presence/absence of CT DNAPL at the base of the unconfined aquifer directly underneath the 216-Z-9 Trench. Results of a 2-dimensional FEFLOW groundwater flow model show that by operating an existing groundwater recovery well in the upper portion of the unconfined aquifer, groundwater entering the deeper pumping well will come only from the lower zone of the unconfined aquifer. The test is scheduled to last for 90 days and a lower limit of 8 mg/l CT in discharge water from the test well was set as the indicator of DNAPL. No information was provided as to how the length of the pumping test and the 8 mg/l CT limit were determined.

In principle, properly designed aquifer pumping tests can be used to identify the presence of DNAPL in contaminated groundwater, if it is present. These types of tests are very dependent upon having detailed knowledge of the hydrogeology and resulting flow paths to place much confidence in the results, especially if the data indicate that no DNAPL is present. Little information was provided in the proposal regarding the conceptual model and the numerical modeling conducted. As a result, the reviewers had to make several assumptions regarding the model (Reviewer #1). One of the reviewers (#1) prepared an alternative flow model, using the

Neuman (1974) solution for an unconfined aquifer with correction for partially penetrating wells and the principle of superposition to demonstrate the complexity of the 3-dimensional flow field (see Figures 1-4 in review #1).

Although the panel considers the proposed use of a pumping test to assess separate-phase CT contamination (DNAPL) to be an interesting and novel scientific approach, the panel raised several technical issues and concerns that must be considered before a decision to conduct the test is made.

- The proposal did not provide a compelling case that the proposed pump test could actually detect the presence or absence of DNAPL in the aquifer. While a positive result may adequately indicate the presence of DNAPL, a negative result would not be definitive, because of significant uncertainties and limitations, and therefore might not be an appropriate technology application.

- Additional 3-dimensional numerical modeling, including particle tracking to estimate travel time from different locations in the flow field and to provide information about whether or not the test well would capture groundwater at the base of the unconfined aquifer from beneath the Z-9 Trench, must be conducted to demonstrate the capture zones of the two proposed pumping wells in three dimensions and the predicted concentrations of CT to be measured over the proposed time of the test using the proposed pumping rate. Results of this modeling may likely require significant re-design of the test parameters and approach.

- The numerical modeling should consider alternative pumping strategies for the pump test, such as intermittent pumping. This is a more sophisticated and complex process from a modeling perspective, but may enhance detecting the presence of DNAPL.

- The modeling must also consider prediction of three ranges of CT concentration, one that indicates DNAPL presence is likely, one that indicates DNAPL is likely to be absent, and one that is "inconclusive," where it is possible that DNAPL may be present. If the breadth of the "inconclusive" range is extremely broad, the value of the test may be extremely poor. Use of an 8mg/L threshold is not considered to be an appropriate scientific approach.

The proposal needs to provide more geological and hydrological information characterizing the project area to enhance the conceptual model to include location of potential DNAPL traps. In particular, previous work done on the structure of the Ringold Mud (either the Vista Engineering cross-borehole seismic survey at the Z-9 Trench or the AVO surface seismic survey by Waddell) should be used to predict the location of the proposed DNAPL (as a trap). More information should be provided in the proposal regarding well locations, screen intervals, lithologic logs, etc.

The proposed project fits well within the DNAPL Conceptual Model Project being performed by Vista Engineering, and it is also integrated with other plans for characterization and remediation of the CT plume in the 200-West Area.

The key risks and uncertainties associated with the proposal are related to 1) the conceptual model, including site heterogeneity, 2) design of the pumping test, and 3) interpretation of the results. It is likely that the proposed pumping test will not lead to substantive answers regarding presence/absence of DNAPL beneath the Z-9 Trench. The basic hypothesis for the proposed pumping test is based upon how accurate the flow modeling is.

Alternatives include:

- Analysis of existing or collection of new geophysical data to better map the location of potential DNAPL traps on the top of the Ringold Mud, prior to conduct of a pumping test;
- Drilling of boreholes to collect depth-discrete core and groundwater samples in conjunction with electronic borehole flowmeter tests to estimate mass flux with depth (this is recommended after better interpretation of DNAPL traps as described in the above bullet).

Implementation Strategy:

- The proposal does a good job of using existing infrastructure and a proven technology, such as aquifer testing, as a cost-effective means of determining the presence of DNAPL in the aquifer. However, the design of the pumping test should be more closely tied to the site conceptual model that identifies a potential DNAPL trap to be sampled.

- The review team recommends additional numerical modeling before a go/ no go decision is made regarding implementation of the pumping test. This modeling should include sensitivity analyses that could evaluate likely plume behavior during the pumping test.

- The proposed test uses a cost-effective approach, but is unlikely to provide conclusive data and thus overall would not be considered to be cost-effective. Additional analyses are needed prior to deciding to conduct the test.

- Identify an appropriate time period for operating the pump test. The proposed 90-day pumping period is likely too short to adequately evaluate presence/absence of DNAPL. No reason for this time period was provided in the proposal

Proposed Performance Metrics:

- There appears to be no baseline for identification and delineation of DNAPL.

- The proposal could benefit from a more detailed definition of the project objective.

- It is unclear as to whether the project could improve the protection of the Columbia River in the future. If the project were successful and able to delineate presence of a DNAPL source, it is not known whether that source could be removed or remediated but if it could, it is possible that there would be some positive impact on the migration of CT to the Columbia River.

- The measurable parameters are time, flow rates, and CT concentrations, which are all easily measured, but do not appear to demonstrate whether the pump test is actually sampling the zone of interest.
- The criteria for establishing whether DNAPL exists does not have a good technical basis and the panel recommends a significant modification.

Reviewer #1

Target Plume/Area: Carbon Tetrachloride / Hanford 200 Area

Proposal Title: CT Contaminant Assessment in the Vicinity of 216-Z-9

Technical Basis of the Proposal:
The proposal describes the plan for conducting a pump test to determine the presence/absence of carbon tetrachloride (CCl_4) DNAPL at the base of the unconfined Ringold aquifer directly underneath the 216-Z-9 disposal trench. A 2 dimensional groundwater flow model was developed by the PIs using FEFLOW to evaluate groundwater flowpaths in the vicinity of the test. Results from the FEFLOW groundwater model show that by operating an existing groundwater recovery well (15-47) in the upper portion of the unconfined aquifer that groundwater entering the deeper test well (15-6) will only come from the lower zone in the unconfined aquifer. The test is scheduled to last for 90 days and a lower limit of 8 mg/L CCl_4 in discharge water from well 15-6 was set as the indicator of DNAPL. Well 15-47 is part of a groundwater remediation system for the 200 West Area that includes 8 other recovery wells and 3 injection wells.

In principle, properly designed groundwater pumping tests can be used to identify presence of DNAPL in contaminated groundwater if it is present. These type of tests are very dependent on having detailed knowledge of the hydrogeology and resulting groundwater flowpaths in order to place much confidence in the result, especially, in cases were the pump test results may be used to indicate that no DNAPL is present. There is very little information in this proposal discussing the conceptual hydrogeologic model for this site and subsequently minimal description of the 2D flow model used as the basis for the design of this test. The reviewer had to make several assumptions regarding the 2D model based on visual inspection of Figure 1 in the proposal: 1) FEFLOW was used to simulate a *vertical* slice of the contaminated aquifer 2) could not determine condition used for top boundary 3) constant head used for side boundaries (ends) 4) no flow boundary used for the bottom. The combination of conditions 1 and 3 greatly constrain the solution and do not account for radial flow towards the well out of the plane of the slice as a result most of the water is forced to come through the ends of the model.

An alternative flow model was prepared using information in the proposal and available in the resource packet provided with the proposal. The model used the Neuman (1974) solution for a pumping test in an unconfined aquifer with correction for partially penetrating wells and the principle of superposition to account for multiple pumping wells. The attached figures show the conceptual model (Figure 1) and results (Figure 2 - 4). Figure 2 shows time drawdown curves for *hypothetical observation wells* located in the lower “E” zone of the unconfined aquifer next to the 2 pumping wells used in the study. Well 15-47 is operated 365 days before well 15-6 is turned on for the 90 day test.

At the end of the test there is approximately 0.2m of drawdown at well 15-47 due to pumping 15-6. The flow field resulting from the alternative model of the pump test

(Figure 3) indicates that the capture zone for well 15-47 may extend from the water table surface to the base of the aquifer between the 2 groundwater wells. Well 15-47 is located between trench 216-Z-9 and well 15-6 and regional groundwater flow ~ perpendicular to a line that connects. Figure 4 shows the simulated hydraulic head for the center of the lower "E" unit of the unconfined aquifer. The assumed natural (no pumping) gradient for the test area was taken to be 0.001 parallel to the x axis based on the water table in ref2. Figures 3 and 4 illustrate the complex 3 dimensional flow field for a multi-well pumping test in an anisotropic aquifer with a non zero natural gradient. The additional pumping wells and injection wells in the actual test area will only make the actual flow field more complex.

Due to the specificity in the proposed interpretation of CCl_4 concentrations from test well 15-6 the reviewer recommends additional numerical analysis of the proposed test using a 3 dimensional groundwater flow model. The 3D groundwater flow model will give a better understanding of capture zones for the wells operating during the test and particle tracking could be used to provide better estimates of travel time from different locations within the flow field.

(Is the project or activity based on appropriate and valid science? What is the technical likelihood of the stated-desired outcome? How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable? What are the risks or key uncertainties in the proposed action(s)? Are there clear examples of alternative ideas or proposals that should be considered? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)

Implementation Strategy:
The proposal does not contain sufficient information to assess if 90 days is long enough for groundwater at the base of the unconfined aquifer beneath Trench 216-Z-9 with CCl_4 concentrations in excess of 8 mg/L to migrate to well 15-6 under the test conditions.

(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)

Proposed Performance Metrics:
Based on the current uncertainty in the calculations that were performed to design the test, it is difficult to say whether or not the proposed pump test represents a significant improvement compared to the baseline or it will improve the protection of the Columbia River now or in the future.

Use of particle tracking with a 3D model of groundwater flow would provide useful information about whether or not well 15-6 would capture groundwater at the base of the unconfined aquifer beneath trench 216-Z-9 and if so how long it might take a packet of water to travel there. CCl_4 concentrations above 8 mg/L can be considered an indicator of DNAPL presence.

(Does the proposed project or activity represent a significant improvement compared to the baseline? Does the project improve the protection of the Columbia River now or in the future? Are there measurable parameters that would document performance? Are these included in the proposal?)

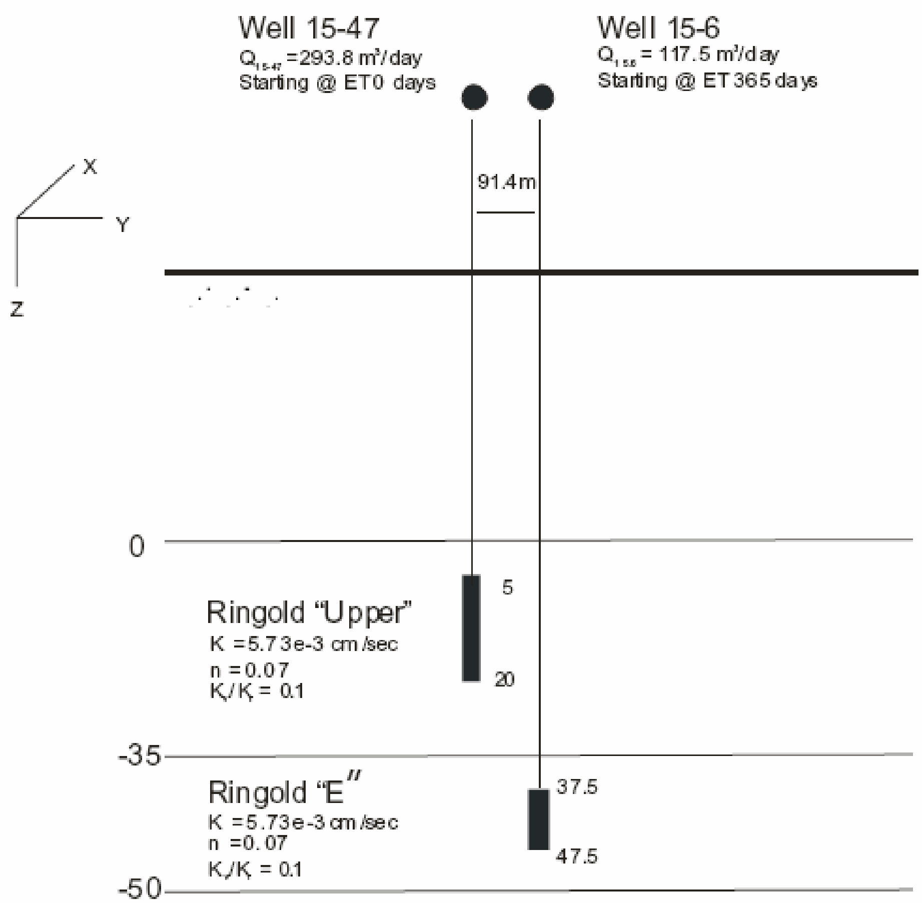


Figure 1 Conceptual model used for calculations in review.

Appendix L

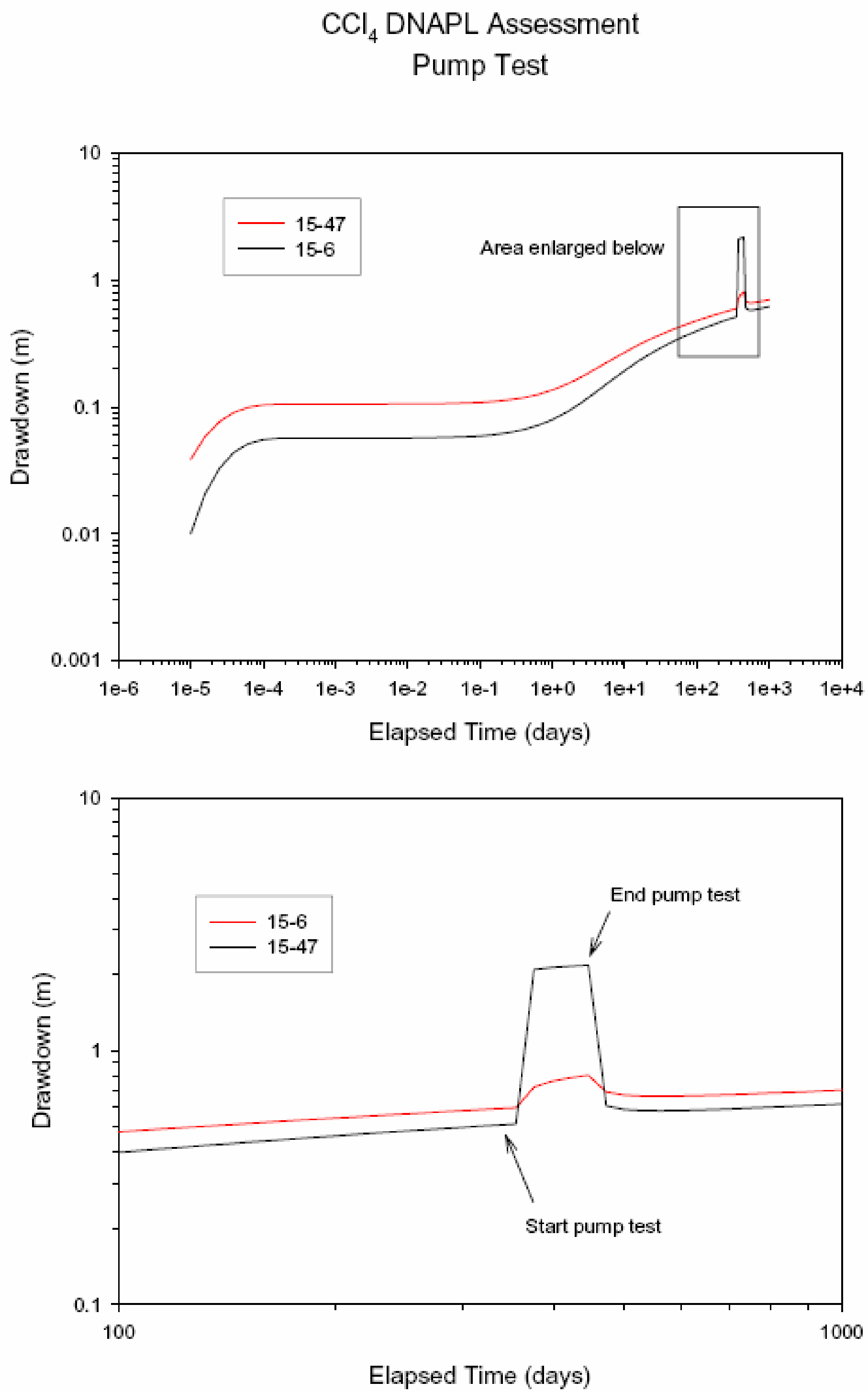


Figure 2 Time drawdown curves.

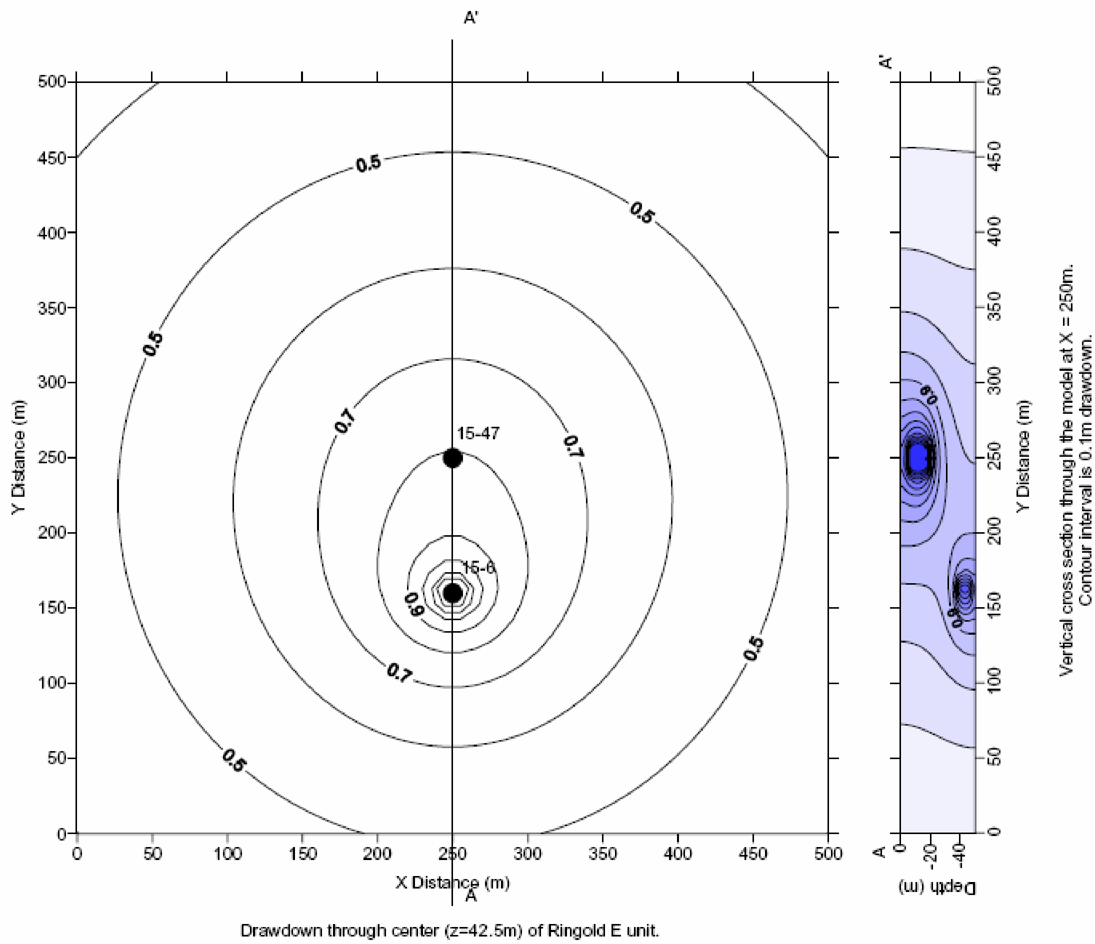


Figure 3 Drawdown map and cross section for pumping test.

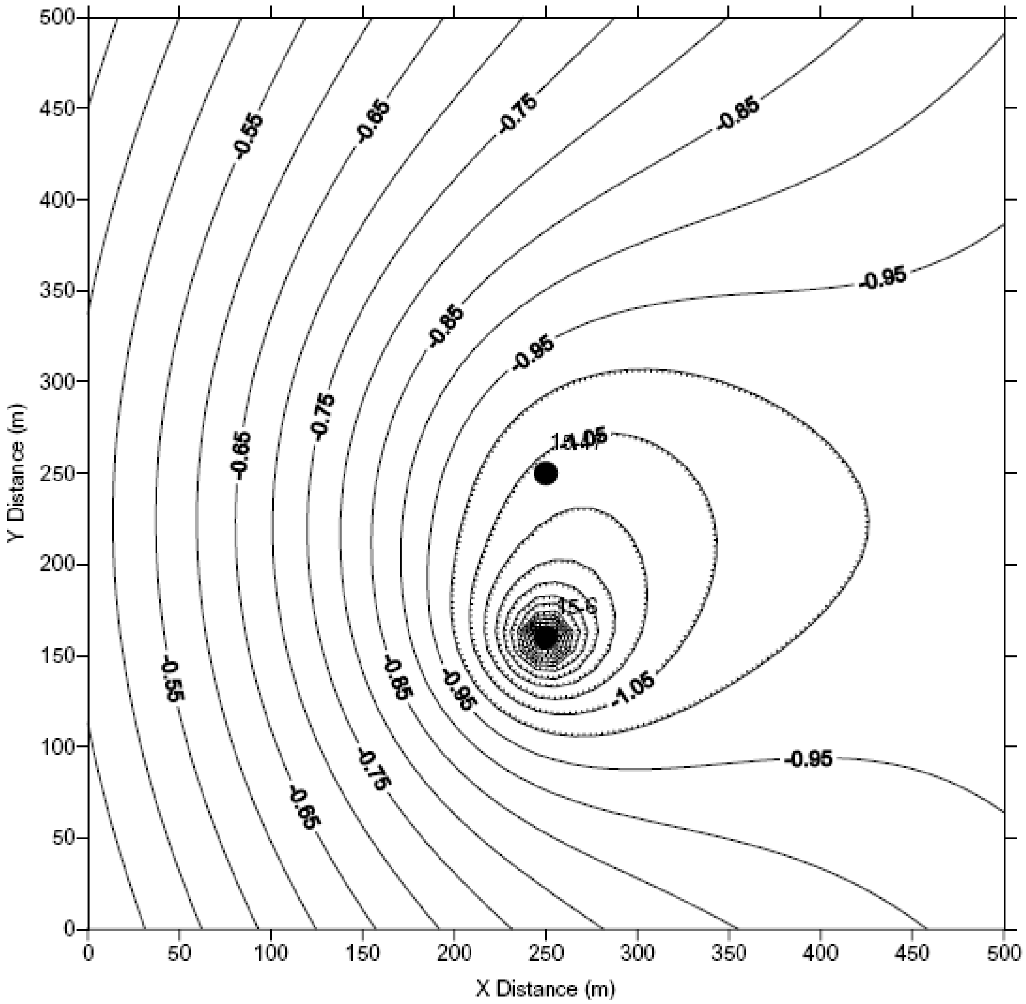


Figure 4 Hydraulic head map for the center (z = 42.5m) Ringold "E" unit.

Reviewer #2

Target Plume/Area: Carbon Tetrachloride/ 200 West Area

Proposal Title: Deep CT Contaminant Assessment in the Vicinity of 216-Z-9

Technical Basis of the Proposal:
(Is the project or activity based on appropriate and valid science? What is the technical likelihood of the stated-desired outcome? How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable? What are the risks or key uncertainties in the proposed action(s)? Are there clear examples of alternative ideas or proposals that should be considered? <u>If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations</u>)

The proposal describes a conceptual model of DNAPL sitting at the base of the unconfined aquifer on top of the Ringold Mud and proposes a pumping test monitoring CT concentrations over time to indicate the presence of DNAPL. The conceptual model assumes that the pumping will promote flow of the DNAPL towards the well within the timeframe of pumping, 90 days. The proposed pumping test is a novel approach to looking for DNAPL below the water table in the 200 West Area at the Hanford site. It is cost-effective, as it is based upon existing infrastructure and a standard technology.

However, there are many uncertainties that exist surrounding this proposed test, and as such, the likelihood of the stated desired outcome is low. Insufficient information has been provided in the proposal to enable a reviewer to estimate the likelihood of the desired outcome. I have concerns about a small simple test like this raising expectations of finding DNAPL. Remember it's like looking for a needle in a haystack. By performing the pumping test, you have increased the size of the needle, but it's still a needle. More information is needed, before this type of test can be conducted effectively.

The project is part of an overall plan to characterize the CT plume to enable improved decision-making regarding a remedial option, i.e. the Feasibility Study. Specific efforts, such as the DNAPL Conceptual Model Project, have been employed to look for DNAPL as a source term for this plume. This has been done in addition to significant efforts at characterization, as well as a pump and treat system and a soil vapor extraction system. A systems approach is definitely underway for this challenging problem.

The proposed approach, in terms of the novel concept, is reasonable and practicable, but I believe the likelihood of success is very low. No information was provided to the reviewers about how the test was designed (e.g., how this particular well was selected for the pumping test, where it is screened, where the top of the Ringold is located vertically, what the topography is on top of the Ringold, how the pumping rate and length of the test were calculated, how the flow field will be impacted by the pumping, where the water that will be analyzed will be coming from, etc.). Identification of a single value that delineates absence/presence of DNAPL is not a valid approach due to the significant uncertainties. Hence, it is very difficult to assess the practicality of the project.

It appears that the pumping well is located to the northeast of the Z-9 Trench. If, however, the dip on the top of the Ringold is towards the southwest, the DNAPL may not migrate to this well within the allotted timeframe. It appears that more information should be gathered about the structure of the proposed DNAPL trap, before a well for such a pumping test could be selected. Either existing geophysical data (cross-borehole seismic at the Z-9 Trench or surface AVO seismic by Waddell) or new geophysical data should be used to predict DNAPL trap locations, prior to design and conduct of the pumping test. Perhaps all of this conceptual model work has been completed, but no detailed information was provided to the reviewers.

The risks to perform this test at this time appear to be too great. More upfront analysis of the groundwater flow field and location of a DNAPL trap needs to be done.

No information was provided on former peer reviews to justify this being an expedited review. This proposal doesn't provide enough detail to enable a supportive review.

Implementation Strategy:
(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work? <u>If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)</u>

There is no problem performing the test. It can be done relatively cost-effectively, because it is based upon existing infrastructure. It is a standard technology. But if there is no value to the test, then it is not cost-effective.

The strategy for implementation should be based upon implementation after identification of an appropriate DNAPL trap, based upon geologic structure.

Proposed Performance Metrics:
(Does the proposed project or activity represent a significant improvement compared to the baseline? Does the project improve the protection of the Columbia River now or in the future? Are there measurable parameters that would document performance? Are these included in the proposal?)

This project, if successful, could improve the protection of the Columbia River, in the future. Measurable parameters for this project are the CT concentrations measured in the groundwater as it is pumped from the well over time. If CT concentrations increase over time, it will be likely that DNAPL is present in the unconfined aquifer somewhere in the vicinity of the pumping well.

It appears that the test produces an answer that either says “there is a high likelihood of DNAPL” or “it is unknown whether DNAPL is present in the unconfined aquifer.” The answer will either be “yes” or “maybe.”

The measurable parameters are simply concentrations and volume of water pumped. There are no metrics to demonstrate from where the water that is to be analyzed is derived from. This significantly limits the usefulness of the test.

Summary Evaluation:
The proposal calls for a novel approach to searching for DNAPL in the unconfined aquifer at the 200 West Area. I applaud the investigators for their ability to propose a cost-effective approach, as it is based upon existing infrastructure and standard technology, to the problem. However, insufficient information was provided to the reviewers: identification of a likely DNAPL trap, construction of the wells to be pumped, limited numerical modeling describing the induced flow field, etc. As such, the reviewer is very concerned that this particular pumping test is not likely to produce the desired results, i.e. identification of DNAPL presence or absence.

There is no information provided about how this particular well was selected, how it is constructed, how close it is perforated to the Ringold Mud, how long the screen zone is, whether the well is located up or down gradient from the predicted DNAPL introduced into the subsurface at the Z-9 Trench, how the proposed pumping rate was selected, whether the test as designed will actually sample the aquifer immediately above the Ringold Mud, etc.

An improved conceptual model, with specific information on the structure of the Ringold Mud, identifying a “low” in its surface “downgradient” from the Z-9 Trench source (i.e. a DNAPL trap) is recommended to justify conduct of the pumping test to produce the desired results. Additional numerical modeling detailing the predicted flow field and evaluating a number of operating scenarios is needed to ensure appropriate test design. In addition, the use of a single cut-off value for presence/absence of DNAPL is problematical. The reviewer is concerned that by performing the test with very little scientific basis for its design, the investigators may severely impact the future use of the pumping test method.

Reviewer #3

Target Plume /Area: Carbon Tetrachloride / Hanford 200 Area

Proposal Title: Deep CT Contaminant Assessment in the Vicinity of 216-Z-9.

Technical Basis of the Proposal:
Is the project or activity based on appropriate and valid science?
Yes. Differences in the mass balance of carbon tetrachloride (CT) believed to have been discarded to three primary sites in the 200 Area of the Hanford site and that which has been removed or remains in the subsurface suggests that the existing conceptual model for the CT plume may be incorrect. The acquisition of additional information that may assist in improving the existing conceptual model is thus important to (i) better define the location of the CT plume; (ii) better understand the potential for existence of a non-aqueous phase liquid (NAPL) form of CT; and (iii) better identify the location of CT NAPL, if it exists. Due to the enormous cost associated with additional direct well drilling, use of existing wells to further evaluate the source of the CT plume in the 200 Area of the Hanford site appears reasonable. Specific objectives of this work include use of existing wells to obtain concentration data from the bottom portion of an unconfined aquifer to better evaluate the existence of NAPL in the saturated zone, and, if it indications support the potential for NAPL existence, its likely location.

What is the technical likelihood of the stated-desired outcome? Poor, as described in the proposal. Unfortunately, the proposal lacks sufficient detail to properly evaluate whether this effort will improve confidence in the conceptual model for the CT contamination in the 200 Area. Both 2-D and 3-D models have been employed to evaluate the behavior of the CT plume; with some results suggesting the potential for a CT NAPL source either in the middle portion of the unconfined aquifer, or, as hypothesized here, in the deep or bottom portion of the unconfined aquifer. While this reviewer believes that the concept behind simultaneous pumping in a shallow-aquifer from well (299-W15-47) and deep-aquifer well (299-W15-6) is rather eloquent, significant concerns exist in whether pumping from of the aquifer will provide sufficient evidence to note the existence of a CT NAPL source. Concerns include: (i) ability of simultaneous pumping from W15-47 and W15-6 to actually separate zones of influence such that W15-6 is effectively able to sample from the target zone of the deep aquifer without sampling from the other potential NAPL source in the middle portion of the aquifer; (ii) ability of W15-6, which is located approximately 300 feet away from the likely source (216-Z-9 trench), to effectively tap into the source NAPL plume – is this well 300 feet downgradient of the source trench? (iii) does sufficient subsurface geology information exist to effectively determine the slope of the bottom confining layer?; (iv) sensitivity analysis of “several different model variables and modeling algorithms” was used in the modeling efforts for two scenarios: NAPL at mid-depth, and NAPL towards the bottom of the aquifer; unfortunately insufficient detail is provided to identify the primary contributors to the observed results – given the site heterogeneity, this reviewer believes that the sensitivity analysis (as employed by the proposal writers) was a very valuable contribution, but that a stochastic, rather than deterministic approach, may best be employed to further evaluate the likely plume behaviors given a statistical distribution for the model parameters; (v) a threshold of 8 mg/L is used as a “rule of thumb” for determining the existence or nonexistence of a NAPL source -- this value appears somewhat arbitrary, given the heterogeneity of the site; i.e., there is no guarantee that NAPL exists even if groundwater concentrations were observed above this threshold level – suggest using results from stochastic simulations to provide confidence intervals for expected concentration ranges with or without the presence of NAPL; and (vi) the proposed time period and method for pumping may be inadequate for a 90 day period (may want to investigate use of intermittent pumping over extended time periods to better understand potential for rebound, especially when combined with depth-discrete sampling over the 4-inch screened interval of well W15-6).

How does the project fit in with the totality of proposed activities for the target contaminant/plume? This effort represents a potentially important component of the overall effort to better identify and refine the extent of the CT plume in the 200 Area.

Is the proposed approach reasonable and practicable?
Yes, although again this reviewer has concern regarding a number of proposed activities, namely (i) the somewhat arbitrary definition for success or failure in the determination of a NAPL source based on 8 mg/L concentration limit (although the proposal does identify that concentrations above 8 mg/L would warrant additional sampling activity to further refine origins of the highest concentration) and (ii) use of constant pumping rates over a short period of time (90 days).

What are the risks or key uncertainties in the proposed action(s)?
Risks/uncertainties include: (i) is the conceptual model for CT plume in the 200 Area correct, or close to correct?; (ii) site heterogeneity causing difficulty in pumping from proposed or intended locations; and (iii) ability to specifically identify location of NAPL source, given use of only two wells pumping from different portions of the aquifer (i.e., the NAPL may have migrated from a different location than that believed in the conceptual model).

Are there clear examples of alternative ideas or proposals that should be considered?
Yes. Employ stochastic modeling to better define likely groundwater concentrations with/without the presence of NAPL. Also, consider employing intermittent pumping activity over periods lasting greater than 90 days.

Implementation Strategy:
Is the sequence and timing of activities appropriate?
Yes.

Can the technology be implemented cost-effectively?
Apparently, although pumping over a 90 day period will likely not answer the questions posed by this proposal

Is the budget and level of effort appropriate for the proposed work?
Yes, although details of the wells, operating costs, etc. are not well described (actually deficient description in this case).

Proposed Performance Metrics:
Does the proposed project or activity represent a significant improvement compared to the baseline?
No. The baseline technology is drilling deep boreholes for collection of groundwater and sediment samples. This proposed effort does not involve additional drilling, but rather use of existing wells to collect groundwater samples.

Does the project improve the protection of the Columbia River now or in the future?
Doubtful. Likely outcome of this effort will be the provision of a slightly improved picture of the CT plume in the vicinity of the 216-Z-9 trench.

Are there measurable parameters that would document performance?
Yes. This effort will result in the production of trend plots showing the changes in CT concentrations over time.

Are these included in the proposal?
Yes.

Summary Evaluation:
Strengths of this proposal include (i) use of an experienced and highly qualified team; and (ii) use of a rather eloquent method of simultaneous pumping to better understand the likelihood of existence and location of CT NAPL sources in the bottom portion of the unconfined aquifer. Concerns include: (i) ability of simultaneous pumping from W15-47 and W15-6 to actually separate zones of influence such that W15-6 is effectively able to sample from the target zone of the deep aquifer; (ii) ability of W15-6, which is located approximately 300 feet away from the likely source (216-Z-9 trench), to effectively tap into the source NAPL plume; (iii) need to employ both sensitivity analysis and a stochastic, rather than deterministic approach, to further evaluate the likely plume behaviors given a statistical distribution for the model parameters; (v) a threshold of 8 mg/L appears somewhat arbitrary, given the heterogeneity of the site; and; (vi) the proposed time period and method for pumping may be inadequate for a 90 day period (may want to investigate use of intermittent pumping over extended time periods to better understand potential for rebound, especially when combined with depth-discrete sampling over the 4-inch screened interval of well W15-6).
Given the preponderance of concerns, this reviewer does not recommend funding without addressing the aforementioned concerns.

Reviewer #4

Target Plume/Area: Hanford: Vicinity of 216-Z-9

Proposal Title: Deep CT Contaminant Assessment in the Vicinity of 216-Z-9

Technical Basis of the Proposal:

Is the project or activity based on appropriate and valid science?

The technical basis for this project was reviewed by a panel of experts in October 2005 and due to the very expensive cost of drilling in this area, a deep pumping test was considered a more economical option to assess whether a deep DNAPL source was present below the 216-Z-9 Trench. This is a reasonable economic decision, but may not lead to a conclusive, scientifically defensible result.

What is the technical likelihood of the stated-desired outcome?

The outcome of the proposed project is to develop data that could confirm the presence of a DNAPL source deep within the aquifer beneath the 216-Z-9 Trench. It is not clear what the data will actually show and it would appear that any conclusions from the pumping test will be largely qualitative in nature. For example, I can envision if a very strong positive signal (i.e. high concentrations of CT) is obtained, perhaps making the inference that a significant amount of CT (perhaps DNAPL) exits in the deeper portions of the aquifer. However, for lower detected concentrations of CT or no detect of CT, what is the conclusive result that can be defended in this situation? No DNAPL? A little DNAPL? The defense will rely on the accuracy of unverifiable groundwater flow schemes and the assumption that groundwater is being drawn from subsurface zones of concern.

How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable?

The project is an extension of an ongoing effort to refine the site conceptual model for DNAPL contamination at the 216-Z-9 Trench area. This project does fit in with the overall activities at this site towards this goal. There was some discussion of the contractor’s other studies at the site and a sense that the proposed pumping test will either confirm or conflict with pre-conceived notions (data supported) about whether DNAPL exits in the deeper subsurface. There should have been more detail of these previous studies in the proposal. Perhaps the previous review panel members (Oct 2005) had access to these data?

What are the risks or key uncertainties in the proposed action(s)?

The risks are that the proposed pumping test will not lead to any substantive answers regarding whether DNAPL exists deep within the aquifer beneath the 216-Z-9 Trench area. This entire endeavor hinges on how well modeled groundwater flow represents actual flow in the subsurface. Modeled capture zones provide a glimmer of how water will flow in the subsurface, but can be wildly misleading and rarely validated. My sense is that the data generated will not indicate a clear answer as to whether DNAPL exists in these deeper portions of the aquifer, only a probable answer (sketchy at best).

Also, if evidence of DNAPL is found in these deeper layers, what is the potential for mobilizing DNAPL further into the subsurface by pumping? If a strong positive signal is obtained, at what point is the pumping test stopped? This scenario should be planned for in advance.

Are there clear examples of alternative ideas or proposals that should be considered? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations).
The alternative is a very expensive drilling/coring strategy that could provide the conclusive information needed but at a steep price, particularly if more than one core is needed.

Implementation Strategy:
(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations).
The proposed pumping test is to be conducted in a previously drilled well that has been reconditioned by the contractor. The placement of the well is, presumably, close enough to the 216-Z-9 Trench area to be able to draw water from the zone of interest. Given that the well has already been drilled, the proposed budget for the pumping test certainly appears adequate.

Proposed Performance Metrics:
(Does the proposed project or activity represent a significant improvement compared to the baseline? Does the project improve the protection of the Columbia River now or in the future? Are there measurable parameters that would document performance? Are these included in the proposal?)
The pumping test purports to be able to sample a defined section within the subsurface in order to evaluate the potential for DNAPL contamination within deeper portions of the aquifer beneath the 216-Z-9 Trench area. There are no performance metrics to assess whether the pumping test is actually sampling the zone of interest and the criteria for establishing whether DNAPL exists in this particular zone are unsatisfying.

Summary Evaluation:
The proposed project is an extension of an investigation that is attempting to refine the site conceptual model for the 216-Z-9 Trench area. A pumping test will be conducted in a re-conditioned well that is near to the Trench area. Apparently, drilling cannot be performed within the Trench area due to exorbitant expense and the fact that the cap on the site will not support a drill rig. In the absence of drilling, a separate review panel recommended that this pumping test be conducted in order to probe whether DNAPL exists in the deeper subsurface beneath the Trench area.
The criteria for the existence of DNAPL will be largely qualitative in nature. If the detected concentration of aqueous CT during the pumping test exceeds a certain percentage of saturation value, then the presence of DNAPL will be inferred. It is not clear that this approach will be

conclusive and these criteria for the existence of DNAPL are unsatisfying. I can envision a positive pumping test for DNAPL, if the DNAPL is present in large amounts. If aqueous CT concentrations are high, it would be reasonable to infer the presence of a large DNAPL source. Perhaps this is the point of the test; to test for a massive amount of contamination. If smaller amounts of the CT are present, the results will be very much less conclusive and indeed speculative. How will dilution be estimated? By modeling? It is difficult to judge how far away the pumping test well is from the Trench area and so I do not know how far water needs to move laterally through the subsurface (if any) and whether the pump is likely to draw water from areas that are not contaminated.

This project needs more detail in order for this reviewer to recommend that it go forward. I fear that the results will only lead to more questions with nothing conclusively demonstrated. The only conclusive way to determine the presence of DNAPL in the subsurface is to drill for it; a very expensive endeavor at this site. So, the question becomes how much is it worth to conclusively demonstrate the presence of DNAPL in the deeper subsurface at this site? If there are other data supporting or contradicting the presence of DNAPL in the subsurface, this should have been outlined in detail in this proposal for the panel to assess just how important this pump test is supposed to be. As described above, this pumping test may not provide the solid, defensible results required for these Columbia River projects.

Reviewer #5

Target Plume/Area: Hanford

Proposal Title: Deep CT Contaminant Assessment in the Vicinity of 216-Z-9

Technical Basis of the Proposal:

1. *Is the project or activity based on appropriate and valid science*? The purpose of the proposed work is to refine the conceptual model and understanding of the source of the carbon tetrachloride (CT) plume at Area 200. This is important for assessing both natural attenuation and active remediation. According to the investigators, the existing Hanford Site CT conceptual model postulates that the majority of the CT resides in the fine-grained layers of the Cold Creek Unit (CCU) directly underneath the waste disposal sites. However, there is a mass balance discrepancy between the amount of CT known to have been disposed at the site and the amount remaining in the subsurface or removed/destroyed since introduction. Furthermore, while the operation of a pump-and-treat system "has removed a large amount of contaminant mass, the >4,000 µg/L contour has expanded in size and now extends more northerly and easterly near the extraction wells." These observations have led to the suggestion that a source of CT may exist deeper in the subsurface below the disposal area. Modeling suggests that, if a deeper source exists, it is probably near the bottom of the unconfined aquifer, not the middle. However, modeling also suggests that a deep source should result in a CT concentration gradient, with concentration increasing with depth. This has not been observed based on well sampling. While the overall evidence indicates that a deep source does not exist, the presence or absence of a deep source is extremely important, suggesting the need to obtain more compelling evidence of its presence or absence. Direct drilling into the zone postulated to contain the deep CT source is not possible, as the waste site is covered by a roof slab that will not support the weight of a drill rig. Even if it were possible, it would be very expensive, on the order of $3.5M. The proposed alternative is to simultaneously pump two nearby wells, one deep and one relatively shallow. By setting the pumping rates to values determined from model simulations, it will be possible to recover in the deep well only water from the zone of the suspected source. If the concentration of CT increases to 8 mg/l or higher during the pumping period, the deep source is indicated and further investigation warranted. If concentrations less then 8 mg/l are observed, the possibility of a deep source is not confirmed and other reasons for the mass balance discrepancy should be considered. The proposed activity appears to be based on appropriate and valid science.
2. *What is the technical likelihood of the stated-desired outcome*? The desired outcome is the creation of a figure in which the concentration of CT is plotted versus time or cumulative groundwater pumped. It is extremely likely that this outcome will be achieved.
3. *How does the project fit in with the totality of proposed activities for the target contaminant/plume*? Current remediation of the CT plume involves vapor extraction and pump & treat. According to the (draft) "Supplemental Activities to Protect the Columbia River Adjacent to the Department of Energy Hanford Site: Management Strategy and Implementation Status" report dated February 2006, for CT in the 200 areas (Attachment 3) proposed technologies include an attenuation parameter study and the installation of deep

recovery wells. Regarding an attenuation parameter study, the report indicates that such a study is "the most relevant project related to the question of carbon tetrachloride migration to the Columbia River from the 200 Area." Furthermore, relative to the attenuation study, a recommendation is made to "…provide supplemental funding to the ongoing Alternative Project that is refining the conceptual model and understanding of the residual carbon tetrachloride sources in the 200 Area." The proposal reviewed here will provide important information that will be used to refine the conceptual model and understanding of the residual carbon tetrachloride sources in the 200 Area." Thus, the project fits well within the totality of proposed activities for the target contaminant/plume.

4. *Is the proposed approach reasonable and practicable*? The proposed work involves pumping two wells at specific rates and measuring CT concentration in the recovered water. The approach is reasonable and practical.
5. *What are the risks or key uncertainties in the proposed action(s)*? The key risks / uncertainties are related to interpreting the results. Interpretation depends on the conceptual model for the site, but the purpose of the proposed work is to improve the conceptual model. This suggests that an iterative process may be required. Furthermore, sensitivity analyses may be very important. The investigators have suggested an increasing CT concentration, to above 8 mg/l, is a key criteria for interpretation. If the concentration of CT increases to 8 mg/l or higher during the pumping period, the deep source is indicated and further investigation warranted. If concentrations less then 8 mg/l are observed, the possibility of a deep source is not confirmed and other reasons for the mass balance discrepancy should be considered. The use of the 8mg/l concentration appears to be based on rules of thumb found in the literature. Can the investigators relate this to the current and alternative (deep source) site conceptual models? How robust is the criteria? In other words, how dependent is it on various model parameters or site conditions? What will the investigators conclude if the CT concentration increases to about 8 mg/l?
6. *Are there clear examples of alternative ideas or proposals that should be considered*? The alternative is direct drilling. Vertical drilling is not possible, because the waste site is covered by a roof slab that will not support the weight of a drill rig. Furthermore, it would be extremely expensive. Is horizontal drilling possible? Even if it is, it would be even more expensive.

<u>If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations</u>) According to the (draft) "Supplemental Activities to Protect the Columbia River Adjacent to the Department of Energy Hanford Site: Management Strategy and Implementation Status" report dated February 2006, this is an expedited review.

Implementation Strategy:

1. *Is the sequence and timing of activities appropriate*? The sequence and timing appear to be appropriate.
2. *Can the technology be implemented cost-effectively*? Yes.
3. *Is the budget and level of effort appropriate for the proposed work*? The investigators request $205,000. According to the (draft) "Supplemental Activities to Protect the Columbia River

Adjacent to the Department of Energy Hanford Site: Management Strategy and Implementation Status" report dated February 2006, approximate funding required to improve the conceptual model was estimated to be $800,000. Thus, the requested amount is well below the total amount recommended for this activity. However, it is assumed that the work involved in this proposal is only a portion of the total work needed to improve the conceptual model. Regarding the specific work proposed, more information would be needed to determine if $205,000 is an appropriate amount. It would also be helpful to know what, if any, other work has been proposed to improve the conceptual model.

If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations) According to the (draft) "Supplemental Activities to Protect the Columbia River Adjacent to the Department of Energy Hanford Site: Management Strategy and Implementation Status" report dated February 2006, this is an expedited review.

Proposed Performance Metrics:

1. *Does the proposed project or activity represent a significant improvement compared to the baseline*? The project will improve the conceptual site model.
2. *Does the project improve the protection of the Columbia River now or in the future*? By improving the conceptual site model, the project will aid in the selection and/or design of future remediation (or monitored natural attenuation), which will improve the protection of the Columbia River in the future
3. *Are there measurable parameters that would document performance*? The measurable parameters are time, flow rates, and CT concentrations. These are all easily measured.
4. *Are these included in the proposal*? Yes.

Summary Evaluation:

The purpose of the proposed work is to refine the conceptual model and understanding of the source of the carbon tetrachloride (CT) plume at Area 200. This is important for assessing the possible use of natural attenuation and/or active remediation at the site. Specifically, the project proposes to confirm the presence or absence of a deep source of CT at the site. Direct drilling into the zone postulated to contain the deep CT source is not possible, as the waste site is covered by a roof slab that will not support the weight of a drill rig. Even if it were possible, it would be very expensive, on the order of $3.5M. The proposed alternative is to simultaneously pump two nearby wells, one deep and one relatively shallow. By setting the pumping rates to values obtained from model simulations, it will be possible to recover in the deep well only water from the zone of the suspected source. If the concentration of CT increases to 8 mg/l or higher during the pumping period, the deep source is indicated and further investigation warranted. If concentrations less then 8 mg/l are observed, the possibility of a deep source is not confirmed and other reasons for the mass balance discrepancy should be considered.

The key risks / uncertainties are related to interpreting the results. Interpretation depends on the conceptual model for the site, but the purpose of the proposed work is to improve the conceptual model. This suggests that an iterative process may be required. Furthermore, sensitivity analyses may be very important. The investigators have suggested an increasing CT concentration, to above 8 mg/l, is a key criteria for interpretation. If the concentration of CT increases to 8 mg/l or higher during the pumping period, the deep source is indicated and further investigation warranted. If concentrations less then 8 mg/l are observed, the possibility of a deep source is not confirmed and other reasons for the mass balance discrepancy should be considered. The use of the 8mg/l concentration appears to be based on rules of thumb found in the literature. Can the investigators relate this to the current and alternative (deep source) site conceptual models? How robust is the criteria? In other words, how dependent is it on various model parameters or site conditions? What will the investigators conclude if the CT concentration increases to about 8 mg/l?

APPENDIX M

In Situ Reactive Nanoporous Metal Phosphate Barrier for Sequestration of Technetium (VII)

Target Plume/Area: Technetium (^{99}Tc) / Hanford 200 Area

Proposal Title: In Situ Reactive Nanoporous Metal Phosphate Barrier for Sequestration of Technetium (VII)

Reviewers: Gene LeBoeuf, Jim Clarke, Rod Ewing, Len Feldman, Baohua Gu, Dawn Kaback, Brian Looney, Thomas Mallouk, Andrew Ramsburg

Summary Evaluation:
The panel recognizes that use of a metal phosphate barrier represents an interesting and potentially promising approach for sequestration of technetium (VII) (^{99}Tc) and other select metals. While the proposal appears to address the spirit of two of the congressionally-mandated technical goals – (i) improve DOE efforts to protect the Columbia River from contaminants migrating from the Hanford Site; and (ii) provide new or supplementary technology – the panel believes that the technology described in this proposal is insufficiently developed to meet the timeline noted in the congressional mandate. As such, the panel does not recommend funding.

Recognized strengths of the proposal include (i) the assembled team of scientists as evidenced by their extensive experience and expertise in development of sequestration materials and excellent publication record; (ii) interesting and exciting science in the proposed materials development and analysis; (iii) discussion of useful geologic analogues to demonstrate the viability of using nanoporous metal phosphates to sequester Tc; and (iv) established working relationship with a commercial vendor (Steward Advanced Materials, Chattanooga, Tennessee) to manufacture materials at commercially-relevant scales.

Specific concerns noted by the panel include (i) the maturity of the technology; (ii) materials science issues; (iii) the effects of adding water to a layered vadose zone where the difference in grain size currently retards gravity-driven flow; (iv) the use of surfactants to deploy nanoporous particles may trigger or enhance contaminant mobility; (v) the volume of nanoporous particles needed to effectively sequester Tc considering the influence of competing electron acceptors (i.e. nitrate and nitrite) and subsurface heterogeneities; and (vi) the delivery of nanoporous particles, in terms of the number of boreholes needed, inadequate subsurface characterization of Tc and the geochemical environment, and subsurface heterogeneity. Additionally, the panel recommends that the DOE field office (Richland Operations Office) consider implementing the sequenced recommendations from the previous peer review of vadose zone technologies to treat ^{99}Tc (WMP-27397). There was consensus on the panel that the proposed deployment of nanoporous particles or any other solid amendment into the vadose zone to form a horizontal permeable reactive barrier is improbable and that other alternatives to address Tc are more appropriate to consider.

Although financial support is not recommended under this particular funding opportunity and for the specific proposed application, the panel believes the assembled team of scientists presents a reasonably strong case to further explore the general development of metal phosphate materials as a potential tool for immobilization of technetium (VII) and other metals. It is in this light that the panel further explored specific areas of concern and made suggestions for improvement. Summaries of these recommendations are noted in subsequent sections of this cover document, while individual reviewer comments appear as appendices to this summary.

Technical Basis of the Proposal:
The proposed use of nanoporous Sn-PO_4 and other metal phosphates (M-PO_4) as the active component of a horizontal permeable reactive barrier within the deep vadose zone is worthy of consideration for a number of reasons. First, it appears to address the spirit of two of the congressionally-mandated technical goals: (i) improve DOE efforts to protect the Columbia River from contaminants migrating from the Hanford Site; and (ii) provide new or supplementary technology, where needed, to identify and solve contaminant migration issues. Second, use of Sn-PO_4 for reduction of Tc (VII) to Tc (IV) appears to be based on sound redox chemistry, and is supported by experimental results, including X-ray absorption near edge spectra/extended X-ray Absorption fine structure (XANES/ESAFS) results reflecting sequestration of Tc (VII) via reduction to Tc (IV) on Sn-PO_4 nanoporous materials. Ongoing work on other M-PO_4 based materials may also prove very useful. Third, the research includes both batch and column experiments on Hanford-like sediments with Hanford groundwater (although origin and composition of groundwater (i.e., extent of contamination) proposed for use in this study is unknown). Further, the study will explore the stability of the Sn-PO_4 materials under variable pH conditions. Fourth, the proposal team is experienced in both synthesis of mesoporous materials for sequestration of radionuclides and metals (Mattigod, Wellman, and Fryxell), and in field remediation delivery methods (Gilmore). Fifth, the potential for Sn-PO_4 and/or M-PO_4 to sequester ^{99}Tc would likely be viewed in a very positive light by regulators and stakeholders that are first interested in sequestering the ^{99}Tc plume (saturated zone or vadose zone), and in the potential long-term performance of this barrier, including irreversibility of the reactions.

Although the general concepts brought forward in the proposal are noteworthy, several critical technical issues remain, as noted below. These issues are divided into five subtopics: (i) integration with other proposed technologies; (ii) site physical and chemical heterogeneity; (iii) materials science; (iv) experimental protocols; and (v) deployment and delivery.

Technical issues for consideration:

Integration with Other Proposed Technologies
- While important to address the vadose-zone contamination in the 200 Area, it is unclear how this project addresses the recommendations for testing, demonstrating, and deploying technologies in the deep vadose zone as noted in WMP-27397. For example, how does this fit in with plans for limiting surface water infiltration, or evaluating the effects of desiccation? (Reviewers 5, 6, 7)

- Describe how nanoporous Sn-PO_4 technology fits into the overall systems approach to contaminant remediation, including analyses of the tank farms. Identify a potential support mechanism for nanoporous Sn-PO_4 (e.g., pump and treat), which would provide a systems approach to treating ^{99}Tc. (Reviewers 1, 5)

Site Physical and Chemical Heterogeneity

- Numerous uncertainties remain regarding both chemistry and influence of vadose- zone heterogeneity on the overall reasonableness and practicality of potential field-scale implementation:
  - The proposal appears to be based on limited data from a single borehole from the BC-Cribs and Trenches site. Since the physical and chemical heterogeneity is likely to vary throughout areas of Tc contamination, data from additional boreholes and laboratory tests should be obtained to enhance characterization of the ^{99}Tc plume. This information can then assist in developing improved experimental protocols to (i) demonstrate the appropriateness of the nanoporous materials selected for ^{99}Tc sequestration; (ii) evaluate the sorption capacity of nanoporous $SnPO_4$ particles; and (iii) address concern that the reductive process could be reversed over time. (Reviewer 2)

  - Provide more thorough discussion of ^{99}Tc geochemistry and the potential influence of nitrate on redox capacity of nanoporous adsorbents. Results of an expert peer review of vadose zone technologies to treat ^{99}Tc (WMP-27397) notes: "Another factor that contributes to the inapplicability of vadose-zone redox manipulation at Hanford is the extreme quantities of co-disposed competing electron acceptors, particularly nitrate…. ^{99}Tc would compete with nitrate for electrons and inhibit the effectiveness of redox manipulation until almost the entire nitrate pool is depleted." Address concern about long-term stability of positively-charged nanoporous Sn-PO_4 particles, including proving the immobilization process to estimate the performance of nanoporous Sn-PO_4 over time. (Reviewers 2, 3, 4, 5, 6)

Materials Science

- The proposal does not consider the significant amount of existing literature on apatite and phosphates, which should be consulted to ensure the appropriate nanoporous Sn-PO_4 technology is used. (Reviewer 2)

- Substantiate proposed claims and attributions of nanoporous Sn-PO_4 material characteristics and abilities (e.g., radiation resistance of phosphate is claimed but not documented; ability of pores to collapse around Tc). (Reviewers 2, 4, 5, 6, 7)

Experimental Protocols

- Experimental approaches described in the proposal should consider expanded discussion/explanation in the following areas:
  - "Hanford-type sediments" are expected to be employed in batch and column experiments. Suggest expanding on description of "Hanford-type sediments" to ensure coverage of the spectrum of sediment conditions where Tc contamination is present. (Reviewer 6)

- Similarly, "Hanford groundwater" is also expected to be employed in batch and column experiments (although Table 1, page 3 of the proposal notes Hanford groundwater was used only in the Cr (VI) experiment). "Hanford groundwater containing appropriate co-contaminants, such as nitrate," should be employed in all sorbent material evaluations. (Reviewer 6)

- The influence of the presence of high concentrations of competing electron acceptors (e.g., nitrate) on sorbent selectivity must also be evaluated (i.e., add details to experimental protocols, including specific items of measurement in batch and column studies, adsorption kinetics, and competitive selectivity experiments); further, no specific performance criteria is established (e.g., what is considered selective?). (Reviewers 2, 5, 6)

- The proposal does not adequately discuss X-ray diffraction (XRD) and transmission-electron microscopy (TEM). (Reviewers 2, 3)

- The unsaturated conditions for the proposed column experiments appear to be greater (~20%) than natural Hanford vadose-zone conditions. (Reviewer 5)

- Consider the long-term stability and effectiveness of nanoporous barriers to sequester ^{99}Tc. Address potential concerns that the pores may not be accessible to ^{99}Tc, because they may tend to be easily clogged by mineral/colloidal materials, dissolved organics, organic polymers (used for injection), and salt deposition during wetting and drying cycles. These issues should be evaluated in laboratory tests using realistic environmental conditions. (Reviewers 2, 4)

Deployment and Delivery

- Delivery methods are explored as a part of this proposal; however, no clear deployment objective is provided and discussion is very limited (primarily highlighting success of TiO_2), and does not appear to address the many challenges associated with delivery of positively-charged particles in a deep vadose-zone situation, including the presence of subsurface heterogeneity and effect of gravity on vertical vs. horizontal flux of injected sorbent solution. (Reviewers 4, 5)

- Although viewed in a positive light within the proposal, the "injected metal phosphate particles with their inherent positive charge characteristic … (attaching) to the mineral surfaces within the soil matrix" suggests that delivery of these positively charged materials to an inherently negatively charged soil matrix may be problematic. Although a portion of the work is devoted to investigation or optimization of delivery methods, few details are provided that describe the proposed method of injection, even within the experimental columns. (Reviewers 5, 6)

- There are two critical issues related to nanoparticle transport that must be answered prior to embarking upon an investigation of how the particles perform in flowing systems. These questions pertain to emplacement of the barrier system and are: (i) What are the transport mechanisms controlling emplacement of the particles under water-saturated conditions?; and (ii) What are the transport mechanisms controlling the long-term performance of the particles? These mechanisms need to be fully understood and described mathematically (i.e., constitutive relationships) before deployment of this technology. These lines of investigation are nontrivial and will require significant commitment of resources of a period of several years (a period which is inconsistent with this call for proposals). (Reviewers 5, 9)

- Determine the area and volume of Tc contamination that should be addressed. (Reviewers 6, 7)

- "Cost and deployment potential of barriers emplaced with horizontal and/or multilaterial drilling" is noted as a work element that will form the scientific basis for the proposed study. However, little to no discussion exists on this topic. Pilot- scale (and eventually full-scale) implementation will require additional testing and design to address outstanding technical issues, such as the impact of subsurface heterogeneity. This proposal should provide the necessary evidence that this technology can be implemented and operated cost effectively. (Reviewers 6, 7)

- Consider the number of boreholes and wells required to adequately address the impact of subsurface heterogeneity on lateral coverage. Because the subsurface flow is directed by gravity, capillarity, and heterogeneity, previous work to establish lateral coverage at Hanford indicates injection wells would need to be installed close together (e.g., 5 meter spacing), which would necessitate potentially drilling thousands of wells to address ^{99}Tc contamination. (Reviewer 7) Further, drilling technology cannot be applied without introduction of significant quantities of fluids and this is not normally accepted by the regulators. (Reviewer 5)

- Consider possible impacts of nanoporous Sn-PO_4 particles with sequestered ^{99}Tc becoming mobile and transporting ^{99}Tc to the groundwater. (Reviewer 4)

- Consider the potential for reduced ^{99}Tc to reoxidize and mobilize. (Reviewer 4)

- Considering Hanford's arid climate, the coarse, deep vadose zone can serve as a capillary barrier. Evaluate the potential impacts of injecting significant quantities of water to the vadose zone. This would be a significant adverse collateral impact in a setting where the water draining away will accelerate the migration of underlying contamination. A conceptual model might be developed to focus on trying to keep water out of the vadose zone, if a capillary barrier is currently stabilizing ^{99}Tc and limiting release. (Reviewer 5)

- Perform demonstration tests to show how the technology can be scaled-up.

- Address concerns regarding the use of surfactants to deploy nanoporous Sn-PO_4 solution into the deep vadose zone. Consider the potential for surfactants to control the water content of the soil. (Reviewer 4)

- The proposal should consider and evaluate alternative technologies for ^{99}Tc sequestration that may provide significant benefit for the vadose zone at less investment: (Reviewers 5, 7)
  - Pump and treat
  - Infiltration reduction through capping or eliminating anthropogenic water sources
  - Desiccation
  - Alternative stabilizing technologies or amendments (e.g., iron oxides)
  - Alternative configurations (e.g., pump and treat with re-injection stabilization)
  - Alternative nanoporous materials that could effectively sequester ^{99}Tc
  - Alternative delivery systems (e.g., blowing nanoporous particles into the vadose zone in gas form)

Implementation Strategy:

- More rigorous testing and evaluation is necessary before field implementation should be considered. Emphasis for the proof-of-principle testing should be on materials science and chemistry (primarily Task 1 objectives and goals). Results of this study should provide the required information to answer feasibility questions regarding large-scale implementation. (Reviewers 1, 2, 3, 5, 6, 7, 9)

- Sn-PO_4 materials may be better suited for ex situ water/wastewater treatment rather than deep vadose zone implementation. (Reviewers 2, 5, 9)

- Suggest inclusion of decision tree to assist in overall implementation of laboratory, bench, and ultimately field-scale deployment. (Reviewers 1, 7)

- The timing and cost estimates appear overly optimistic as the activities required for full-scale deployment or the sequence have not been clearly identified. (Reviewers 1, 4, 7)

- Direct costs do not include costs associated with the nanoporous material synthesis or lab-scale and intermediate-scale utilization. (Reviewers 7, 9)

- Budgeted costs are not compared with other potential remediation technologies. Specifically, the total ^{99}Tc plume area is estimated as 0.25 km^2 (2005 Annual Report: 200-UP-1 Operable Unit, GW, p. 2.9-1); how much, and what is the associated cost of nanoporous metal phosphate material that must be employed to sequester the known (or estimated) quantity of ^{99}Tc? Typically, 10s to 100s to 1000s of times the theoretical amounts are needed for real-world deployments to overcome heterogeneity and uncertainty. (Reviewers 6, 7)

- Proposed timeframe is too optimistic. Because pump and treat systems are successful at removing ^{99}Tc from the groundwater, there is no current threat of ^{99}Tc contamination to the Columbia River and vadose transport and release is occurring slowly. However, this is not justification for no action. Treating the groundwater and vadose zone for other contaminant threats might provide time to adequately develop nanoporous technology before implementation. There is no need to rush implementation of an immature or potentially ineffective or risky technology. (Reviewer 9)

- Consistent and appropriate units for cost estimates need to be identified and maintained (e.g., cost per volume).

Proposed Performance Metrics:

- The proposal provides only a limited discussion of performance metrics for using nanoporous $SnPO_4$ to sequester ^{99}Tc. If a new proposal is prepared, it should be peer reviewed for specific and clear performance metrics. (Reviewer 5)

- The proposed objective to design an in situ permeable reactive barrier to sequester ^{99}Tc in the vadose zone is premature and unrealistic for the stated goals. This overoptimistic objective has the potential for substantial harm to DOE, because it implies to the public and regulators that this technology has a high potential for success and that the investment will provide enough information to allow design and deployment. (Reviewers 5, 7)

- Potential stakeholder concerns about the stability of the $Sn\text{-}PO_4$ sorbents and the potential for reversibility are reasonably well covered in the stability testing program; however, no specific performance criteria are provided (what is considered stable?; what are the time scales of the stability experiments and how can these time scales be extrapolated to decades or centuries?). (Reviewer 6)

- Proposal should discuss the risk reduction potential of nanoporous $Sn\text{-}PO_4$.

- Nanoporous $Sn\text{-}PO_4$ cannot be properly monitored as proposed without long-term groundwater monitoring.

- Because the research group has been working on similar technology for more than a decade, the proposal should include discussion of previous experience. What are some of the applications for which their materials were used or not used in the past, and why?

- Address concerns about over-promising how well the technology would perform. (Reviewers 4, 5, 7)

- The proposal provides no basis for its claim that the technology can provide immobilization of ^{99}Tc for "geologic time." Define objectives in terms of flux reduction and meeting specific goals instead of complete immobilization over geologic time.

- The proposed study requires better definitions of success.

Reviewer #1

Target Plume/Area: 200 Area and Tank Farms – Hanford, WA

Proposal Title: In Situ Reactive Nanoporous Metal Phosphate Barrier for Sequestration of Technetium (VII)

Technical Basis of the Proposal:
(Is the project or activity based on appropriate and valid science? What is the technical likelihood of the stated-desired outcome? How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable? What are the risks or key uncertainties in the proposed action(s)? Are there clear examples of alternative ideas or proposals that should be considered? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)

Let me begin by noting that some very interesting and innovative research is being proposed by a strong team. However, there are major uncertainties associated with the feasibility, schedule and cost of installing an extensive horizontal barrier deep in the vadose zone.

The proposed technology is immature and still at the bench scale level. Major uncertainties exist and the schedule that is proposed is unrealistic.

It appears that not much thought has been given to the steps needed to get to full scale deployment, assuming that would be a good thing to do.

The proposal would benefit from inclusion of a decision tree.

Implementation Strategy:
(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)

The timing and cost estimates are unrealistic and I don't think the activities that would be needed to get to full scale deployment nor the sequence have been clearly identified.

Proposed Performance Metrics:
(Does the proposed project or activity represent a significant improvement compared to the baseline? Does the project improve the protection of the Columbia River now or in the future? Are there measurable parameters that would document performance? Are these included in the proposal?)

There is no basis to answer the above questions. Very little is provided with respect to performance metrics for what is proposed and beyond to full scale technology deployment.

While this proposal does address very interesting and innovative research it is just that – research. Furthermore, I am not convinced that full scale deployment of a horizontal PRB of a large area extent, deep in the vadose zone would be a good idea. How would it be monitored and maintained? How does it fit into the total remediation system that would very likely include engineered surface covers over the sources (tanks, cribs, etc.)? In fact is installation of horizontal subsurface barrier that has major uncertainties a better approach compared to surface barriers, of known ability to reduce infiltration that can be monitored and maintained?

Summary Evaluation:
This strikes me as a possible solution to a very different kind of problem. I see potential for use in above ground applications such as ex-situ groundwater treatment, perhaps as part of a pump and treat approach, but the scale of the proposed application here presents serious challenges. Also, it would be good to know how this type of PRB would perform compared to conventional vertical PRBs with respect to performance and cost in a shallow groundwater application.

I recommend that the proposing team identify more feasible applications with other potential sponsors (NSF, DOE Office of Science, DOD, EPA etc.). The proposed work is interesting and innovative but not suited, in my opinion, to the Columbia River Protection program needs.

Reviewer #2

Target Plume/Area: Tc plumes at the Hanford site: 200 Area

Proposal Title: In Situ Reactive Nanoporous Metal Phosphate Barrier for Sequestration of Technetium (VII)

Technical Basis of the Proposal:

In evaluating the technical basis of this proposal, I have reviewed not only the proposal, but also looked at a number of the supporting publications.

General Comments:

The P.I.s have presented an innovative idea for handling/mitigating the mobility of Tc in plumes at Hanford. The idea may hold promise, but it is much too early to evaluate the probability of successful development and implementation. Thus, my overwhelming impression is that the state-of-knowledge of the structure of the nanoporous materials, the specifics of how this material will interact with the TcO_4, and the stability and long-term behavior of the NP-SNPO/Tc are not well enough known to embark on this project as presently proposed. I suggest that much more attention be focused on the work outlined in Task 1, as this would provide a better basis for the work proposed in Task 2. Much more work needs to be completed on the properties of the material before one can properly assess whether NP-SNPO could be an effective barrier to the migration of Tc. The characterization of the material is very limited. As an example, the same TEM micrograph of the NP-SNPO is used repeatedly in the proposal and publications – with little evidence of a systematic TEM examination. The presence and distribution of the pores is not evident in Figure 1 of the proposal or the supporting publications. In fact, it will require some rather sophisticated electron microscopy techniques to characterize the nanopores in this material. The use of x-ray absorption spectroscopy (XAS), that is the XANES and EXAFS, is also limited. Figure 2 of the proposal does not clearly indicate "the oxidation of NP-SNPO with concurrent reduction of the target metal contaminant." They do not indicate which elemental edge is being presented in the figure. The experimental determination of the K_d for the different elements are not well described, and the conclusion that the metals are incorporated into the nanopores is not well supported.

Very specifically, there is little or no discussion of the chemistry of Tc and how it will interact with the surface sites of the nanoporous material. The sorption/reduction of negatively charged species onto surfaces of minerals or synthetic materials is particularly problematic, as these surfaces generally have a negative charge. Under Task 1, the P.I.s indicate that the nanoporous materials will be tailored to have a positive surface charge to mitigate mobility in the subsurface. I would like to have more details on how the surface of the NP material is tailored to have and maintain a positive charge. This is an important accomplishment that needs to be well documented in this proposal. This problem could be approached, in part, by the use of computational chemistry. In fact, I suggest that the entire proposal should have simply focused on the work to be done as part of the "Sequestration Kinetics and Mechanisms" section of Task 1, prior to the initiation of Task 2.

The PIs should also take advantage of the data (although limited) in the literature. A few papers in my files include:

S. El-Wear et al. (1992) Sorption of Technetium on inorganic sorbents and natural minerals. *J. of Radioanalytical and Nuclear Chemistry*, vol. 157, 3-14.

K.E. Guerman et al. (1995) Experimental study of Tc-99 sorption by the basic minerals and rocks during the disposal of nuclear wastes. *Radioactive Waste Management and Environmental Remediation*, 713-722.

S. Madhavi et al. (2005) Synthesis and crystallization of macroporous hydroxyapatite. J. of Solid State Chemistry, vol. 178, 2838-2845.

Although these (and other) papers provide limited data – they are useful for placing the present work into context.

Finally, the proposal must directly address the sorption/reduction capacity of the material vs. the amount of Tc that must be "captured" and the long-term behavior and potential for later release of the Tc. One must also realize that the use reactive permeable reactive barriers is a relatively new technology (1990s) and that we need much more data in order to predict long-term performance. The proposal would benefit from some discussion of the successes and failures in the use of permeable reactive barriers. This would be, in part, the focus of the work proposed under Task 2, but as I have previously indicated, Task 2 should be built on the foundation of the knowledge developed in Task 1.

A number of these issues mentioned above are captured by the list of proposed study topics in section #9, "Scientific Basis of Project"; however, there are very few details in the proposal on how this work would be done.

Specific Comments:

There are a number of statements that are made for which the evidence is minimal or absent:

a. It is not obvious that the Tc-99 is sequestered within the nanopores of the material.

b. There is only limited evidence that nanoporous phosphate materials enhance the inherent capability of these materials for the sequestration of redox-sensitive radionuclides.

c. There is no evidence presented that "phosphate particles with their inherent positive charge characteristic will attach to the mineral surfaces within the soil matrix." I think that we need more details on the use of the "anionic template during synthesis."

d. There is no demonstration that there is "sorption to nanoporous ligand sites".

e. There is no evidence of the "reduction of the oxidized contaminant to less-soluble valence states by coupled reaction of nanoporous metal oxidation."

f. The general applicability of NP-SNPO to so many different elements: Tc, Cr and Np raises the question of the exact sorption mechanism(s). Is it the same for all of these elements? The chemistry of these elements is so different that one expects that there would be very different mechanisms and rather different results for each.

g. Finally, the "Description of the Problem" is actually a statement of conclusion, "The deployment of a nanoporous material barrier would irreversibly sequester and significantly reduce the inventory of available Tc-99 that may contribute to groundwater contamination." This is simply not a well supported statement – given the data cited in the proposal.

Implementation Strategy:

To me it is not evident that the material will perform as described or designed. The implementation sequence and schedule are logical, but the presumption is that the material will work as designed. Unless this is demonstrated (with a fundamental understanding of the mechanisms) on the bench scale, and further tested in column experiments, it is premature to begin to design or implement field scale tests. Again, Task 2 addresses a part of this concern by the use of column experiments and NP stability testing, but this part of the program must be built on several years of effort devoted to Task 1. I do not believe that both can be done on the aggressive schedule as outlined in section 25.

Another important issue with implementation is whether the NP-SNPO particles can be effectively placed in the path of the Tc-plume. The P.I.s refer to the successful injection and placement of TiO_2 particle suspensions, but there is not enough detail to evaluate whether this would also work for the NP-SNPO particles.

Proposed Performance Metrics:

If the NP -SNPO performs as proposed, if the material can be put in place as proposed and if other chemical reactions in the system (e.g., due tovariations in groundwater compositions) do not compromise the performance of the material, then this method may successfully reduce the mobility of the Tc.

The most obvious performance metric would be to monitor the ground water compositions on both sides of the permeable reactive barrier.

Summary Evaluation:

Although the P.I.s have worked on these materials for some time (previously under OCRWM), limited information is available on the properties and behavior of the material.

At best, I would recommend only funding a smaller scale program that focuses on the material properties with a specific focus on material-Tc interactions. This is essentially the Task 1 section of the proposal.

Reviewer #3

Target Plume/Area: Technetium/Deep Vadose Zone/200 Area

Proposal Title: In Situ Reactive Nanoporous Metal Phosphate Barrier for Sequestration of Technetium (VII).

Technical Basis of the Proposal:
The proposal describes an innovative method for Tc sequestering. The idea of using a high-area, nano porous material with the desired chemical properties provides a new approach to the Tc problem.

The scientific basis requires significant further exploration as described below.
1. Materials Characterization – proposal provides useful and illuminating preliminary characterization. More experimental work is required. More samples explored by TEM, sufficient to accumulate statistically meaningful data are highly desired. This should yield distribution of nano pore sizes, nanoparticles size.

2. The EXAFS data needs to be quantified. The conversion of 2+/4+ states needs more extensive data quantification.

3. The presentation of the materials science needs significant expansion. The descriptions need amplification and should be more complete.

4. The uniqueness of this particular chemistry needs to be explained. Do other nano porous materials work? Is there something unique about the "nano" property, other than the large surface area? Surface chemistry?

5. Quantitative analyses: What is the Tc saturation density? How much material/quantified? Cost estimates?

6. More sophisticated analysis of the chemistry.

Implementation Strategy:
Implementation strategy research is not appropriate at this point. The first emphasis should be on the materials science and the chemistry, with implementation an important factor for future consideration.

Proposed Performance Metrics:
Baselines do not exist – this is a new technology. The authors need to define their metrics in light of their understanding of the overall objectives.

Summary Evaluation:
Does not meet the specific needs of the call. There is a high potential for developing important basic science that could underlie an innovative sequestering technique. The science proposal should be developed, and presented in a competitive scientific funding forum. Such a proposal should include a list of milestones including systematic temperature dependence, time dependence, coverage measurements, etc.

Reviewer #4

Target Plume/Area: 200 Area and Tank Farms, Hanford

Proposal Title: In situ reactive nanoporous metal phosphate barrier for sequestration of technetium (VII)

Technical Basis of the Proposal:
(Is the project or activity based on appropriate and valid science? What is the technical likelihood of the stated-desired outcome? How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable? What are the risks or key uncertainties in the proposed action(s)? Are there clear examples of alternative ideas or proposals that should be considered?

This proposed work is to develop metal-phosphate nanoporous sorbents as barrier materials for removing Tc-99 from contaminated groundwater. The barrier will be deployed by injecting metal-phosphate nanoporous materials into the vadose zone sediments. Metal phosphate sorbents, especially nanoporous tin phosphate (NP-SNPO), have been demonstrated to sequester Tc-99 within the nanopores in laboratory batch equilibrium studies. The proposed approach appears technically sound, and the project team is strong and has been working in this area for a number of years. However, some key risks and uncertainties (see below) have not been fully understood and considered in this proposal, and the technical likelihood for field application of this technology is questionable. The following key risks and uncertainties ought to be considered before the deployment of this technology.

1. The sorption capacity and selectivity have not been demonstrated or evaluated under realistic and relevant environmental conditions (i.e., in the presence of competing ions, especially at high nitrate concentrations found at the site). The sorption capacity and selectivity are likely much lower than those shown in Table 1.

2. The effectiveness of NP-SNPO nanoporous materials to sorb Tc is largely attributed to their high specific surface area (because of the nanopores). However, this also creates problems that these pores may not be accessible but easily be clogged by mineral/colloidal materials, dissolved organics, organic polymers (used for injection), and salt deposition (e.g., NaNO3, calcium carbonates, silicates, etc.) during wetting and drying cycles. In other words, under realistic environmental conditions, these nanopores are likely plugged well before Tc even gets there. It is thus critical that these processes be fully evaluated in simulated laboratory experiments under repeated wetting and drying cycles.

3. Mechanisms of Tc sequestration in NP-SNPO have been attributed to redox-coupled reactions, i.e., the reduction of Tc(VII) to Tc(IV) species, which are much less soluble. However, under vadose zone environment, reduced Tc(IV) may become reoxidized and therefore mobilized. Although PIs indicated that nanopores may collapse upon sorption of Tc (so that Tc could be "permanently" fixed), this has not yet been demonstrated. Additionally the presence of nitrate

could be a problem for reductive immobilization of pertechnetate. This may present a long-term stability issue and should be carefully examined.

4. Another related issue is the potential mobilization of injected NP-SNPO nanoparticles with sequestered Tc. Literature data indicate that NP-SNPO nanoparticles are negatively charged unless surfaces are modified with cationic surfactants (although PIs claim that these nanoparticles are positively charged so that they should be strongly retained by the sediment).

5. No cost data were provided. It is important to evaluate the economic feasibility for manufacturing NP-SNPO materials for large-scale deployment, as compared with other alternative barrier materials.

6. The statement that "these metal phosphate particles are expected to continue to perform as a barrier over geological time spans" is an over-sale, given above considerations. Alternative approaches such as the use of Fe- or Al-oxyhydroxides, iron nanoparticles etc. may be considered (as the baseline technology) because of their relatively low cost and availability. These materials have long been demonstrated to be effective in removing Tc (as pertechnetate), and should be considered as baseline technologies for comparisons.

Implementation Strategy:
(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work? <u>If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)</u>

The sequence and timing of activities looks appropriate, but I would recommend more rigorous testing and evaluation be performed before field deployment, as noted above. The technology can be implemented, as it has been demonstrated by the placement of TiO_2 particle suspensions in Hanford-type sediments (no details were given).

The proposed budget appears reasonable. The scale of the column experiment is not clear, and no field work is to be performed.

Proposed Performance Metrics:
(Does the proposed project or activity represent a significant improvement compared to the baseline? Does the project improve the protection of the Columbia River now or in the future? Are there measurable parameters that would document performance? Are these included in the proposal?)

This depends on how the baseline technology is defined. Authors used "pump-and-treat" as the baseline technology, which may not be appropriate because pump-and-treat usually refers to treatment in saturated zones. No cost data were provided, it is hard to judge if it is economically feasible.

The project may improve the protection of the Columbia River, but it is unlikely to meet the congressional mandate, given the current state of science of this treatment technology.

Summary Evaluation:
Although the proposed approach is a novel idea, the technical feasibility for short-term field application is questionable, and it is unlikely to meet the congressional mandate. Some key factors such as risks, uncertainties and costs of materials need to be carefully considered and determined before the deployment of this technology.

Reviewer #5

Target Plume/Area: 200 Area, including BC Cribs and Trenches, S, SX, T, and TX Tank Farms

Proposal Title: In Situ Reactive Nanoporous Metal Phosphate Barrier for Sequestration of Technetium (VII)

Technical Basis of the Proposal:
(Is the project or activity based on appropriate and valid science? What is the technical likelihood of the stated-desired outcome? How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable? What are the risks or key uncertainties in the proposed action(s)? Are there clear examples of alternative ideas or proposals that should be considered? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)

The science of producing nanoporous metal phosphate to treat radionuclides in water or wastewater is appropriate and valid science. However, trying to apply the technology for this specific Hanford subsurface problem is not appropriate. The technical likelihood of it ever being deployed as a full-scale remedial solution is extremely low.

I question why tin phosphate was selected. The proposal says it can be applied over wide pH's, even greater than 9. This is not a likely scenario for the Hanford vadose zone and as such doesn't provide any advantage. I believe the technology may be better applied for water and wastewater treatment. I recommend the PI pursue this pathway for application of the technology. Has there been an alternatives materials analysis? There were two references to work emplacing Ti nanoparticle suspensions into Hanford sediments, but no reference was provided. I would like to see more about this work. Why aren't these particles being further studied? What about amorphous Al and Fe hydroxides, which also have positive charges and high surface areas.

There was little focus on studying how the particles are held up in the formation where they are injected and thus don't migrate downwards given a large flushing event that could possibly occur at rare times in the future. It was stated that because the particles are positively charged, they won't move. But has that really been demonstrated or is it planned for demonstration? Focus seemed more on Tc sequestration rather than particle movement. Demonstration of the ability to get the particles into the formation and keep them there must be part of any new proposals to other funding programs.

There could be concern regarding flushing of Tc downward during emplacement of particles due to fluids added to the vadose zone. Please refer to the technical assistance report on Tc in the vadose zone, funded by Fluor in 2005: WMP-27397 Rev 0, EVALUATION OF VADOSE ZONE TREATMENT TECHNOLOGIES TO IMMOBILIZE TECHNETIUM-99 The subject document can be accessed on OSTI's website: http://www.osti.gov/bridge/.

If the sequestration process is reductive, there will be an issue with co-contaminants, such as nitrate, which at BC Cribs and Trenches is present at the same depths as the Tc at concentrations as high as 100,000 ppm. Almost all of the reductive capacity of the materials would be used to reduce the nitrate. Thus, huge quantities of materials would be required for injection.

I am not sure I understand the unsaturated and saturated column experiments. Is the material emplaced under unsaturated conditions and then is the column saturated to add Tc or to see if the Tc is mobile? The unsaturated conditions proposed seem to be much greater (~20%) than natural Hanford vadose-zone conditions.

What does the SPFT provide that can't be ascertained through leaching of the column? It seems less realistic. Why does the SPFT use nitrogen gas? Vadose-zone conditions will not be reducing.

I have no information about how the project fits with any other proposed activities for the target contaminant/plume. DOE needs to develop a systems approach for this problem.

The proposed approach is not reasonable or practicable. They compare the costs to that of other permeable reactive barriers being studied for implementation below the water table immediately up-gradient of the Columbia River. This is a very different situation where you are treating a relatively narrow plume flowing horizontally just before it enters the river rather than "building" a horizontal permeable reactive barrier, which would have to cover the entire vadose zone plume area to prevent downward migration.

The major risk with funding this project is the setting of expectations that a practicable solution is being developed. The uncertainty of whether the technology could ever be deployed for this problem is extremely high.

In 2005, Fluor Hanford funded an expert panel to evaluate alternatives for this problem. The panel recommended further investigation into the use of desiccation in combination with surface covers as a method to minimize downward migration of Tc in the vadose zone. It was felt by the panel that desiccation had the greatest likelihood for an active practical implementation. Andy Ward has done a modeling study at BC Cribs and Trenches to demonstrate how surface covers could successfully reduce impacts in the groundwater from Tc. Another option would be to remove pipelines or other potentially "leaking" sources that continue to add fluid to the vadose zone. Other alternative materials are described above.

Implementation Strategy:
(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work? <u>If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)</u>

The sequence and timing of activities is appropriate for an EM Science project. It is a proof of principle project.

The technology cannot be implemented cost effectively for this problem at Hanford. There is no detail as to how the technology would be implemented, but this is a big omission. How big are the Tc plumes? How big would the barrier be? For example, BC Cribs and Trenches is about 22 acres in size and a barrier that large would be cost prohibitive to build. In addition, little is known about the depth of penetration of Tc in the vadose zone at BC Cribs and Trenches. Without better site characterization, it would be difficult to implement a remedial action. In addition, there is no information provided about how far the particles can move into the formation during injection. As such, there is little information about the required spacing for the injection wells. This is where the costs would escalate to the unreasonable.

There is one mention of the use of horizontal and/or multilateral drilling to emplace the material, but these drilling methods cannot be used at Hanford, because of the difficult drilling conditions and the desire to drill without drilling fluid.

It is possible that this technology could be implemented at some other site, but not at Hanford for this problem.

Proposed Performance Metrics:
(Does the proposed project or activity represent a significant improvement compared to the baseline? Does the project improve the protection of the Columbia River now or in the future? Are there measurable parameters that would document performance? Are these included in the proposal?)

I don't know if there is a baseline for this problem, so I cannot comment on it being a significant improvement. However, I don't believe it will ever be implemented as a remedial solution for this problem. If it could be implemented cost effectively, it could improve protection of the Columbia River in the future.

I see few measurable performance objectives in the proposal. However, if a new proposal is submitted to DOE Office of Science, it should be written with more technical detail with measurable parameters, which could include delivery and longevity issues. Although as a first step, it might not deal with delivery. It seems to be a technology looking for a problem; it's just a proof of principle test.
Summary Evaluation: This project should NOT be funded under this program, as the technology cannot be implemented as a viable solution for the problem described. In addition, the status of the technology development is in the research stage and would fit better within the DOE Office of Science. Lastly, the technology may be more appropriate for treatment of water and wastewater above ground. The PIs should consider submittal of a competitive proposal to the DOE Office of Science, but would need to substantially rewrite the proposal and provide more technical detail, building upon previous research conducted by the proposal team.

The purpose of the funding provided by Congress was to quickly show an impact on reducing contaminant entry into the Columbia River. Before this proposal could be considered for funding, a preliminary cost analysis for application of this technology at any one of the above sites would have to be done to provide a technical basis. The issue with this proposal is the viability of the implementation of the technology for Hanford vadose-zone problems as described. The proposal doesn't deal with the implementation issue at all, but studies the chemistry.

Proposal is not well written as many of the claims aren't backed up with real data or explanations. Proposal needs more technical detail.

My biggest concern with funding this work is that it will promote expectations that a viable approach for sequestration of Tc in the vadose zone specifically at Hanford is being developed. Funding of this proposal would not be an appropriate use of the money received from Congress to help protect the Columbia River in a timely fashion.

Reviewer #6

Target Plume /Area: Technetium / 200 Area and Tank Farms, Hanford, WA

Proposal Title: In Situ Reactive Nanoporous Metal Phosphate Barrier for Sequestration of Technetium (VII)

Technical Basis of the Proposal:
The use of metal phosphate materials as an active component of a permeable reactive barrier appears to possess promise for a number of reasons. First, it appears to at least address the spirit of two of the congressionally-mandated technical goals: (i) improve DOE efforts to protect the Columbia River from contaminants migrating from the Hanford Site; and (ii) provide new or supplementary technology, where needed, to identify and solve contaminant migration issues. Second, use of tin-phosphates for reduction of Tc (VII) to Tc (IV) appears to be based on sound redox chemistry, and appears to be supported by experimental results, including X-ray absorption near edge spectra/extended X-ray Absorption fine structure (XANES/ESAFS) results reflecting sequestration of Tc (VII) via reduction to Tc (IV) on tin-phosphate nanoporous materials. Ongoing work on other metal-phosphate based sorbents may also prove very useful. Third, the proposal team is experienced in both synthesis of mesoporous materials for sequestration of radionuclides and metals (Mattigod, Wellman, and Fryxell), and in field remediation delivery methods (Gilmore). Fourth, the potential for Sn-PO4 and/or M-PO4 to sequester ^{99}Tc would likely be viewed in a very positive light by regulators and stakeholders, especially in terms of its potential for service as a very long-term component of a reactive barrier, including potential increased resistance to reversible reactions.

Although the *general* concepts brought forward in the proposal are noteworthy, several critical technical issues remain as noted below.

Technical issues for consideration:

- While important to address the vadose zone contamination in the 200 area, it is unclear how this project fits "in with the totality of proposed activities for the target contaminant/plume." For example, how does this fit in with the limitation of surface water infiltration/desiccation of the vadose zone proposals? Does this have applicability to saturated zone emplacement? What is the probable zone of influence for material injection wells? How many wells are required, and what are their costs? Specific comparisons to existing technologies, especially when used in the light of back-of-the-envelope estimates, will be extremely useful. Statements such as "Currently, no technology exists that can effectively sequester ^{99}Tc in the vadose zone and prevent its migration into the underlying aquifer" appear to ignore other technologies described in the report "Evaluation of Vadose Zone Treament Technologies to Immobilize Technetium-99", Fogwell and Petersen, September 2005.
- The proposal lacks sufficient detail to support many of the statements noted therein (for example, what direct evidence exists that the materials are indeed nanoporous? (side note: Steward Advanced Materials refers to these materials as "mesoporous" on more than one occasion in Appendix C: Material Manufacturing Support); what evidence exists that the

matrix "collapses" about ^{99}Tc upon sorption?). Although this reviewer recognizes the limitations imposed by the format of proposal, the "science" behind the statements are often not supported by either experimental evidence or cited literature, even when one considers Appendix A: Scientific Basis for Proposed Testing.

- Numerous uncertainties remain regarding both chemistry and influence of vadose zone heterogeneity on the overall reasonableness and practicality of full-scale implementation of this program.
  - Chemistry issues
    - Potential interference and sorption of other vadose zone impurities, possibly resulting in clogging of the pore structure (2 nm). How will clogging/loss of sorption capacity over extended time frames be evaluated (an important issue for any reactive barrier)?
    - Potential influence of nitrate on redox capacity of nanoporous adsorbents. Results of an expert peer review of vadose zone technologies to treat ^{99}Tc, edited by Peterson and Fogwell (September 2005), note: "Another factor that contributes to the inapplicability of vadose-zone redox manipulation at Hanford is the extreme quantities of co-disposed competing electron acceptors, particularly nitrate….^{99}Tc would compete for electrons and inhibit the effectiveness of redox manipulation until almost the entire nitrate pool is depleted."
    - Although viewed in a positive light within the proposal, the "injected metal phosphate particles with their inherent positive charge characteristic … (attaching) to the mineral surfaces within the soil matrix" suggests that delivery of these positively charged materials to an inherently negatively charged soil matrix may be problematic. Although a portion of the work is devoted to investigation or optimization of delivery methods, few details are provided that describe the proposed method of injection, even within the experimental columns.
  - Heterogeneity issues
    - Delivery methods are explored as a part of this proposal; however, discussion is very limited (primarily highlighting success of TiO_2), and does not appear to address the many challenges associated with delivery of positively-charged particles in a deep vadoze zone situation, including the presence of subsurface heterogeneity and effect of gravity on vertical vs. horizontal flux of injected sorbent solution.
- Experimental approaches described in the proposal require expanded discussion/explanation in the following areas:
  - "Hanford-type sediments" are expected to be employed in batch and column experiments. Suggest expanding on description of "Hanford-type sediments" to ensure coverage of the spectrum of sediment conditions where Tc(VII) contamination is present.
  - Similarly, "Hanford groundwater" is also expected to be employed in batch and column experiments (although Table 1, page 3 of the proposal notes Hanford groundwater was used only in the Cr (VI) experiment). First, "Hanford groundwater" should possess the full range of expected concentration of potentially interfering substances such as oxygen, nitrate, etc. (it was unclear from the proposal and the conference call whether the "Hanford groundwater" used to date possess this full range). Second, "Hanford groundwater" should also be employed in all sorbent material evaluations (especially the target metal of interest, Tc (VII)).
    - The influence of the presence of high concentrations of competing electron acceptors (e.g., oxygen and nitrate) on sorbent selectivity must also be evaluated (i.e., add details to

experimental protocols, including specific items of measurement in batch and column studies, adsorption kinetics, and competitive selectivity experiments). Further, no specific performance criteria is established (e.g., what is considered selective?).

- Discussion of employment lacks sufficient detail with respect to delivery methods, areal extent of targeted plume (i.e., required volume of injection), monitoring program, and definition of "success" (i.e., performance objectives). The 2005 Annual Report: 200-UP-1 Operable Unit, GW, p. 2.9-1 notes an areal extent of the ^{99}Tc plume at 0.25 square kilometers, or 25 hectares. This is a very large area to apply potentially expensive synthesized nanomaterials. The 5 kg material estimate noted during the conference call would result in a planar density of 200 g per hectare (or 20 mg per m^2). Assuming a very conservative estimate of 5 m thickness of the barrier, and further assuming that the material could be applied in a uniform fashion in the deep vadose zone using horizontal drilling techniques (a rather optimistic assumption), suggests a volumetric density of 4 mg of active barrier materials per m^3 of aquifer material. Given this density, it is extremely unlikely that all of the ^{99}Tc could intersect the sorbent, and that failure of the barrier would almost be assured.
- Potential stakeholder concerns about the stability of the tin-phosphate sorbents and the potential for reversibility are generally addressed in the stability testing program; however, no specific performance criteria are provided (what is considered stable?; what are the time scales of the stability experiments and how can these time scales be extrapolated to decades or centuries or tens of centuries?).

Implementation Strategy:

- Sequencing and timing is inappropriate for this work. It appears to this reviewer that the proposed combination of basic materials science with intermediate scale deployability represents a square peg trying to be placed in a round hole – it just does not fit. Rather, the assembled team appears better suited for further exploration of the science of materials development and evaluation (with advisement on deployability). Given the number of unknowns, and the extreme complexity of the deep vadose zone environment, it is unreasonable to expect the proposed work to be able to meet the stated objective to "design an in situ permeable reative barrier to be used in the vadose zone to sequester Tc-99 contaminated groundwater". Instead, the likely outcome will be a realization that significant further study is required prior to deployment (not necessarily a bad result). Premature deployment of this technology could very likely lead to failure in the field – not because the concept is incorrect, but, rather a lack of understanding of the interplay between material properties and the environment within which the material will be exposed. Failure in this setting, however, could significantly affect potential future deployments of this technology.
- Budgeted costs appear reasonable for a fundamental science effort, but not for a combination of science and intermediate scale application.
  - Direct costs do not include costs associated with the nanoporous material synthesis or lab scale and intermediate scale utilization.
  - Budgeted costs are not compared with other potential remediation technologies. Specifically, the total ^{99}Tc plume area is estimated as 0.25 km^2 (2005 Annual Report: 200-UP-1 Operable Unit, GW, p. 2.9-1); how much, and what is the associated cost of

nanoporous metal phosphate material that must be employed to sequester the known (or estimated) quantity of ^{99}TC?

- "Cost and deployment potential of barriers emplaced with horizontal and/or multilaterial drilling" is noted as a work element that will form the scientific basis for the proposed study. However, little to no discussion exists on this topic. Pilot-scale (and eventually full-scale) implementation will require additional testing and design to address outstanding technical issues, such as the impact of subsurface heterogeneity. This proposal should provide the necessary evidence that this technology can be implemented and operated cost effectively. Currently, this approach is just a "proof of principle" test. *Bottom line: results of this study should provide the required information to answer feasibility questions regarding large-scale implementation.*

Proposed Performance Metrics:

- Performance metrics (other than some general discussion on material stability) do not appear to be specifically addressed in the proposal. A more detailed description of specific performance objectives is required.
  - The proposal essentially constitutes a science effort aimed at further developing and evaluating metal-phosphate materials for sequestration of select metals. As such, the performance metrics should focus on specific measurements that will help test the hypotheses of interest.

Summary Evaluation:

The use of a metal phosphate barrier as the active component of a permeable reactive barrier within the deep vadose zone provides for a potentially promising approach to long term containment and treatment of ^{99}Tc plumes at the Hanford site. Further, the scientific team identified in the proposal represents an outstanding group of recognized and well-established scientists in this field, and the potential for the proposed materials to provide long term sequestration of ^{99}Tc is noteworthy. Nonetheless, employment of these sorbents poses a number of challenging issues/questions that are not sufficiently addressed in the proposal. As such, the technology described in this proposal is insufficiently developed to meet the timeline noted in the congressional mandate. Specific comments on technical basis, implementation strategy, and performance metrics follow.

Reviewer #7

Target Plume/Area: Tc / 200 Areas

Proposal Title: In Situ Reactive Nanoporous Metal Phosphate Barrier for Sequestration of Technetium (VII)

Technical Basis of the Proposal:

General

This project is a new concept – thus it is not fully consistent with previous peer reviews and recommendations. It generally fits in to a systematic "blended" approach to the challenge of Tc at Hanford – essentially based on the premise that Tc is present in large amounts, Tc in its likely chemical form is long lived and relatively mobile, and that much of the Tc is present in the vadose zone underlying various cribs and tanks at Hanford. Selection of this "high risk" (of failure) (and probable extreme-cost) technology is "justified" by the proposers through the statement that there are "no alternatives." This neglects the fact that infiltration reduction (e.g., by eliminating process and non-process wastes/water, leaking water and fire lines, leaking cooling lines etc.) and capping would have a major impact on Tc release from the vadose zone. Other technologies such as desiccation, while also highly uncertain, may provide significant benefit for the vadose zone at less investment. The annual report documents that pump and treat in the shallow groundwater was quite effective for Tc. While not necessarily desirable, pump and treat might be easily accomplished at a lower price than "tons" of custom nanoparticles injected into closely spaced wells over many acres.

Real-world success of the proposed technology in the Hanford vadose zone is unlikely. This is unfortunate since the proposed science is very interesting and exciting and the research team is of a very high quality. They have an outstanding track record of excellent research and publication.

Because of the high degree of technical risk, this research appears to be better suited to a basic science program like ERSP, rather than a small Congressionally mandated program (whose focus is on documentable improvement in the protection of the Columbia River). While the case can be made that the Tc is a future threat to the river, limited amounts of Tc have made it to the groundwater and measurable groundwater Tc is immediately beneath or adjacent to large sources. If Tc is sufficiently mobile to justify a hypothesis that it threatens the Columbia River in any substantive manner, then why has it not moved through the vadose zone and generated a large groundwater plume (like carbon tetrachloride or tritium or even ^{129}I)? The 200 Area is miles from the river and this technology is speculative, at best – the proposers are optimistic in all of their descriptions and they gloss over potential problems of deployment – these problems will dominate the potential viability of the technology. As a result, the proposal does not read like an objective science proposal, but an attempt to fund interesting basic science research by a tortured linkage to this call.

Specific comments:

Research to focus primarily on mechanisms of Tc interaction – sorption and a nonparticle specific redox reaction. This is an appropriate science objective but provides limited progress toward the stated goals.

The proposal notes that nanoparticles have been shown to be deployable in Hanford sediments and that they do not show much back pressure and they distribute relatively evenly. How far? If it is optimistically 5 meters, than many closely-spaced injection wells will be needed when applied to several hectares. The particles are noted to be positively charge as planned (so they will become part of the sediment) but they also are alleged to be deployable and migrate long distances. Were such positively charged particles of the proposed size tested in the previous experiment for which the optimistic interpretation was provided?

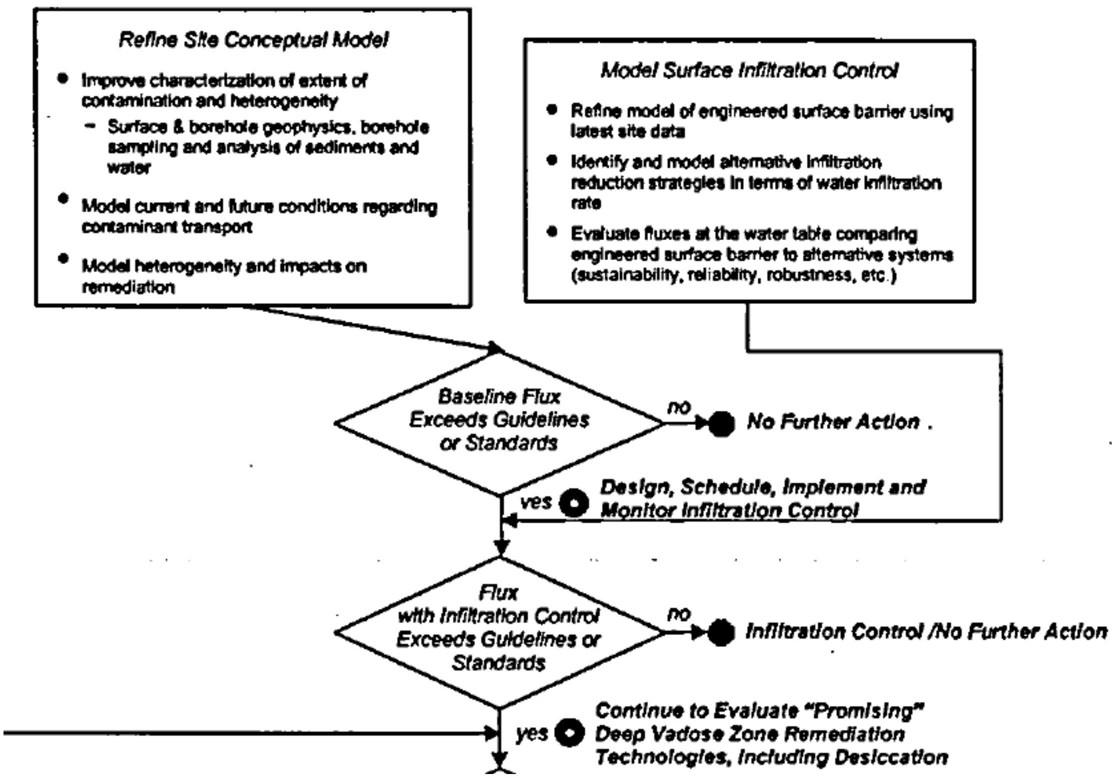
How much water is needed? This would be a significant adverse collateral impact in a setting where the water draining away will accelerate the migration of underlying contamination.

The geologic statements about compatibility (i.e. analogs) and the existence of an existing commercial partner that has manufactured previous particles based on PNNL research is a significant strength of the proposal – but the typical costs for such production (is it $/Kg or $/ton) are not provided.

The proposal states that the cost would be expected to be similar to other barrier deployments at Hanford (e.g., apatite). This is improbable. The deployment at the 200 area would be deeper in a more complex drilling environment. Since the proposed technology is a vadose zone barrier, a laterally extensive plane of amendment would need to be deployed. This would be difficult in a setting where the injected fluid is controlled by gravity, capillarity and geology. A liquid based well to well dipole control concept (while theoretically conceivable) is unlikely. Thus, a large number of wells would be needed. If wells were on 10 m spacing (optimistic) than about 90-100 wells into the deep vadose zone would be needed to treat 1 hectare. On more realistic 5 m spacing, about 350-400 wells/hectare would be needed. Based on the background information, many hectares need to be treated, and there is a lot of interfering culture and old waste facilities in the way of the deployment (further increasing costs). In the previous peer review (WMP-27397) using approximately 5 m spacing, over 3500 wells would be needed to treat just the BC Crib target area. The cost of particles is also a potential factor. With no data provided in the proposal, I assume that the cost of the nanoparticles will be significantly greater that the cost of the commodity chemicals used in the alternative shallow barriers at Hanford. All of this adds up to best case costs of $100s to 1000s of millions unless there are major unexpected breakthroughs or findings (the kind that would come from a basic science program). A back of the envelope calculation for just the drilling using optimistic numbers ($100 to $400 per foot drilling, 1000 to 3500 wells, 100 to 200 ft deep) results in costs of $10 million to $280 million.

Few of the issues and uncertainties in the 2005 Independent Expert Panel Assessment of technologies for vadose Tc (WMP-27397) were considered or addressed in the proposal. Related to vadose reactive and sorptive barriers, these issues include, fluid delivery, extreme chemistry associated with brine disposal, competing electron acceptors, avoiding excess injection water, the need/probability for capping, uncertain geology and contaminant distribution, etc. Relatively specific discussion of each of these topics is provided in the referenced report and each of these should be objectively considered in developing a proposal to address Tc in the Hanford vadose zone. Most important, the flowchart (see excerpt below) in the previous peer review had two steps before considering in situ vadose treatment. Spending a large amount of funding on a later stage without the earlier steps appears to be inconsistent and potentially wasteful.

Excerpt of earlier independent panel recommendation:



Additional specific comments:

Task 1 – outstanding proposal for testing variations of the proposed particles and their sorption and interaction with Tc. Does not necessarily address issues of co-contaminants such as high nitrate that will potentially interfere with the Tc reduction.

Task 2 – Intermediate scale testing is reasonable as a step toward goals. But this work at the small lab column scale is unlikely to provide data that are useful for full scale design over many meters in a heterogeneous environment.

A design concept based on estimating dose based on total activity divided by maximum nanoparticle sorption capacity is naïve and optimistic. A result of such a calculation that 5Kg deployed over 22 acres is not reasonable – typically 10s to 100s to 1000s of times the theoretical amounts are needed for real-world deployments to overcome heterogeneity and uncertainty.

The tasks as described provide limited information on the stated goal of examining the impacts of polymers and deployment aids, and the goal of cost and viability of alternative deployment and access methods (spacing and geometry of wells).

Implementation Strategy:
The lab research proposed has almost no potential to reach the stated objective:

"With the proposed schedule, {the proposers} expect to develop this technology to the extent that it will be available for potential deployment at the site in support of the CERCLA and single-shell tank cleanup decisions made for the Hanford Site."

This overoptimistic objective has the potential for substantial harm to DOE because it implies to the public and regulators that this technology has a high potential for success and that the investment will provide enough information to allow design and deployment. I do not believe that the research, focused on small scale details of nanoparticle structure, sorption, and surface chemistry, will provide the necessary data on large scale production, handling, access needs, matching of particle deployment to contamination, adverse impacts (e.g., large quantities of water injection), and response to real-world complexities (e.g., high nitrate).

Proposed Performance Metrics:
Limited. See above

Summary Evaluation:
An interesting and potentially exciting science project about nanoparticles but with limited applicability to a program that is focused on protection of the Columbia River. High risk of not providing an applicable technology – this program would fit better in ERSP. Risks are both to DOE (by implying uses and applications that are unlikely) and to nanotechnology (by not meeting typical nanotechnology rigor and having marginal potential for meeting claimed goals). If the basic research showed a breakthrough, then the follow on effort would be more justified. If the project is funded, a more objective and less partisan scientific linkage to the vadose objectives and Columbia River objectives that carefully addresses the issues identified above and in previous peer reviews should be required. This would minimize the potential for overselling the technology to regulators and stakeholders. I recommend rejection in the context of the supplemental funding.

Reviewer #8

Target Plume/Area: 200 Area and Tank Farms, Tc (VII).

Proposal Title: In Situ Reactive Nanoporous Metal Phosphate Barrier for Sequestration of Technetium (VII).

Technical Basis of the Proposal:
(Is the project or activity based on appropriate and valid science? What is the technical likelihood of the stated-desired outcome? How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable? What are the risks or key uncertainties in the proposed action(s)? Are there clear examples of alternative ideas or proposals that should be considered? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)

This proposal builds on a very successful R&D program at PNNL to design new mesoporous materials for sorption of a variety of contaminants. This work has been successful in removing mercury and other heavy metals from simulated aqueous waste streams, and is now being studied for application to toxic metals in high oxidation states, such as Cr(VI) and Tc(VII).

The team of Fryxell, Mattigod, and coworkers has strong expertise in the synthesis of porous materials and has demonstrated that these materials have very high sorption capacity for metal-containing contaminants. The proposed use of mesoporous Sn(II) phosphates for remediation of Tc(VII) is based on sound chemical principles because one expects a redox reaction that will result in formation of an immoble Tc(IV) oxide. This has been confirmed in preliminary tests using Tc(VII) solutions in sodium bicarbonate and in Hanford ground water. X-ray absorption measurements confirm the expected redox reaction.

Implementation Strategy:
(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)

There are several chemical issues that have not been resolved in these prelimary tests and are not addressed in the proposal. One is potential interference from nitrate and nitrite, which are present in much larger quantity than pertechnetate in the contaminant plumes. This problem is described in detail in the DOE report, *Evaluation of Vadose Zone Treatment Technologies to Immobilize Technetium,* S. W. Peterson and T. W. Fogwell (Fluor Hanford, September 2005), pp. 3-3 – 3-5. It needs to be verified that the porous tin phosphates will adequately sorb and reduce Tc(VII) in simulated vadose zone material and ground water that contains these contaminants at realistic levels. Another problem is that not all of the ^{99}Tc in Hanford tank wastes is present in the +7 oxidation state. It is well known that the tanks contain soluble Tc species in lower oxidation states. Because the chemical nature of these reduced species is not precisely known, it is difficult to make realistic simulants that might be used in the kinds of column tests proposed to test the efficacy of the porous metal phosphates. However this is a real issue that will affect the performance of the permeable reactive barriers in the field.

The proposal does not address the issue of emplacement of the permeable reactive barrier. One of the PI's (Gilmore) has expertise in this area, and this problem may be considered beyond the scope of this proposal. However, in considering the end use of the technology it is important to have at least a tentative plan for emplacement at the depth that will be needed. In the same vein, I did not find an estimate of the materials cost for a porous tin phosphate permeable reactive barrier on the scale that will be needed at the site. This estimate is relevant to the realistic consideration of this technology because other low cost barrier materials (such as zero valent iron) may be effective at lower cost.

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Reviewer #9

Target Plume/Area: 200 Area and Tank Farms, Tc (VII).

Proposal Title: In Situ Reactive Nanoporous Metal Phosphate Barrier for Sequestration of Technetium (VII).

Technical Basis of the Proposal:
(Is the project or activity based on appropriate and valid science? What is the technical likelihood of the stated-desired outcome? How does the project fit in with the totality of proposed activities for the target contaminant/plume? Is the proposed approach reasonable and practicable? What are the risks or key uncertainties in the proposed action(s)? Are there clear examples of alternative ideas or proposals that should be considered? <u>If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations</u>)

This proposal is focused refining a metal phosphate nanotechnology to sequester TcO_4^- in the deep vadose zone. The proposed effort would build on the success of previous work by identifying: the kinetics and capacity of Tc-99 sequestration; the stability of the Tc-metal oxide complex; and potential strategies for establishing a vadose zone barrier (i.e., a permeable reactive barrier). At the core of the project is the interaction between tin-phosphate or titanium-phosphate nanoparticles (~150 nm) and technetium species. The PIs have a record of developing these (and similar) particles and the PIs are capable of determining the particle characteristics which provide greater/more selective sequestration (first part of Task I).

Determination of the binding mechanisms and kinetics is a worthy pursuit that should lead to a more accurate understanding (and prediction) of when and how sequestration may fail. Knowledge of the binding kinetics is critical to barrier design, yet it is unclear how the data from task I will be integrated into subsequent experiments. The proposal could more clearly describe how the effort will address/test/determine issues related to selectivity and competition. While it is recognized that the experiments outlined in the proposal are an important first step in determining the effects of competitive interactions, model systems of a limited number of ions may not be adequate to fully explore competitive effects which may occur in the extreme chemistries of Hanford contamination.

Activities under task II aim to investigate barrier emplacement (i.e., the transport and deposition of the nanoparticles) and barrier stability. Both unstaturated and saturated column experiments are proposed using sediments from the Hanford area 200 site. Efforts in Task II lack a clearly stated objective -- the reader is left wondering how the nanoparticles will be deployed. The proposal (page 5) appears to suggest that the particles will be introduced by saturating the pore space. The description of Hanford groundwater or Hanford sediments is ambiguous. The PIs are encouraged to quantify the important/relevant characteristics of these waters and sediments when describing the proposed effort. General characterizations may be available in DOE reports and may allow the PIs to also characterize the spatial variability in water and sediment properties over the large 200 area.

While the reactivity studies outlined in Task II (column experiments with emplaced particles) are an important confirmatory line of investigation, there is only a modest potential that these experiments will result in data which are useful to management of the Hanford site. The proposed effort (and Task II in particular) would be substantially strengthened by including a PI/co-PI with expertise related to transport in porous media. There are two critical issues related to nanoparticle transport which must be answered prior to embarking upon an investigation of how the particles perform in flowing systems. These questions pertain to emplacement of the barrier system and are: (1) what are the transport mechanisms controlling emplacement of the particles under water-saturated conditions and (2) what are the transport mechanisms controlling the long-term performance of the particles. These mechanism need to be fully understood and described mathematically (i.e., constitutive relationships) before deployment of this technology. These lines of investigation are nontrivial and will require significant commitment of resources of a period of several years (a period which is inconsistent with this call for proposals).

The technical practicability of the proposed technology is highly uncertain. While the preliminary data are quite promising in terms of long-term sequestration in batch systems, serious questions will remain (even upon completion of the work outline in the proposal) regarding the emplacement of nanomaterials. In fact, it is unclear if the PIs have even contemplated how many particles will be necessary to capture and sequester the Tc-99 plume for the next 10, 25, 50, or 100 years. A simplified mass balance calculation should be preformed with existing data on the estimated Tc-99 plume mass and batch data for distribution coefficients (conservative solid-liquid ratios). This type of calculation could be refined throughout the project and would make an excellent metrics for go/no-go decisions. Refinements to the calculation could include: thickness of the barrier assuming equilibrium (i.e., once the surface of the sediments is covered with the particles); thickness given batch kinetic data; thickness given the in situ reactivity data, etc.

Implementation Strategy:
(Is the sequence and timing of activities appropriate? Can the technology be implemented cost-effectively? Is the budget and level of effort appropriate for the proposed work? If this is an expedited review these comments can utilize the previous peer review(s) and reflect if the activity is being implemented in accordance with those recommendations)

The project is designed such that the first 7 months are focused on optimizing the particles and determining the sequestration mechanism(s). The subsequent 9 months are devoted to experiments aimed at identifying the reactivity in columns containing Hanford sediments. This is a highly linear format/schedule that limits both portions of the overall investigation. The study would be much more sophisticated if it included nanoparticle transport experiments that informed the optimization studies. The proposed effort considers particle optimization to only include greater capacity and selectivity in batch systems. In the field, however, optimization must include transportability – and will likely involve a compromise between factors controlling the sequestration per gram of nanoparticles and the number of nanoparticles per gram of soil.

The budget seems to be somewhat salary heavy for 16 months worth of studies. Of the $700K requested, about $20K is requested in supplies. It is, however, unclear who's time (and how much of it) is being charged to the project to produce the ~$300K labor charges.

The personnel have a history of working together and producing publishable results with DOE funding. It is unclear if Fruchter, who is listed as Project Manager, will be involved in the project as there is no CV.

There is no estimate or supported consideration given to the cost of technology implementation, however, this should not be considered to be a shortcoming of the technology or proposal. The technology requires laboratory based studies (i.e., the proposed effort) to identify key parameters (rates, emplacement mechs, etc.) which will likely control implementation costs.

Proposed Performance Metrics:
(Does the proposed project or activity represent a significant improvement compared to the baseline? Does the project improve the protection of the Columbia River now or in the future? Are there measurable parameters that would document performance? Are these included in the proposal?)

There is not a baseline technology for treating Tc contamination in the deep vadose zone in the 200 area. There is a baseline technology for sequestration – capping and desiccation. Current efforts in some areas of the site are focused on containing the contamination (through use of pump and treat) once it reaches the groundwater table. The proposed effort offers significant potential, but at a relatively high risk. There will be important questions related to the emplacement (and potential migration) of the barrier system that will persist long after this 16 month investigation. The transport of nanoparticles in the environment is an emerging field with very few studies focusing on subsurface transport. Those studies that do focus on the transport of nanoparticles in the subsurface primarily focus on the saturated zone. Studies on transport of nanoparticles in the vadose zone are rare. This represents an opportunity for the PIs to conduct years of cutting edge research and potentially develop a novel approach to Tc-99 treatment. The technology, however, represents a high risk for these same reasons. These nanomatrials are sinks for Tc-99. Strict hydraulic control will be required to ensure that the particles do not impact the downgradient environment if/when they become mobile. Hydraulic control means that the pump and treat system will need to remain active. The proposed effort begins to consider the longer term fate of the nanomaterials, but does not adequately consider the issues of nanoparticle transport.

Summary Evaluation:
The PIs have proposed to investigate tin and titanium phosphate nanoparticles for the sequestration of Tc-99 in the deep vadose zone at the Hanford site. The laboratory research aims to move a relative immature technology toward field deployment. Use of nanoparticles for long term sequestration may hold great promise and deserves further investigation. At present, the technology represents a high risk and it is unclear that the proposed research will significantly

alter this status due to a combination of the remedial process being extremely complex and an experimental design which limits interpretation and scale-up.

The research is broken into two tasks which focus on (1) building a nanoparticle which can sequester more Tc-99, and (2) long-term sequestration in flowing systems. Efforts in Task 1 are important, but should move well beyond being a derivative of the PIs prior efforts (e.g., Mattigod et al. 2005 ES&T). The development, characterization, capacity, kinetics and long-term binding of Tc should be considered as a basic science proposal. Task 2 considers important questions, but fails to address the most critical issue – mechanistic description of nanoparticle transport during emplacement and performance phases. A limited number of treatability type column experiments conducted with soil from one location in area 200 will not produce the data necessary to develop the mechanistic descriptions of nanoparticle transport that is required to advance this technology to the field.

The team has experience in designing and creating the nanomaterials. In addition they have a publication record together which demonstrates they work well together and can deliver on investment. The team is ideally positioned to conduct the experiments described in Task I (nanoparticle optimization). The experiments described in Task II are seriously flawed and the entire Task should be revised to focus on nanoparticle transport. The portion of Task II relating to the long term fate of the nanomaterials containing Tc is important and could, perhaps, be conduced using nanoparticles 'loaded' in batch experiments.

Overall this project does not meet the criteria for funding under this call. The idea of using the nanomaterials to sequester Tc is attractive, and the PIs should focus on demonstrating the capability from a fundamental science prospective. Design, characterization and testing of new nanomaterials may be better suited to basic science programs. Materials developed under this type of investigation may find application in above ground treatments, and the PIs are encouraged to consider ex situ treatments.