INNOVATIVE TECHNOLOGY
Summary Report

DOE/EM-0499

In Situ Redox Manipulation

Subsurface Contaminants Focus Area

Prepared for
U.S. Department of Energy
Office of Environmental Management
Office of Science and Technology

January 2000

INNOVATIVE
TECHNOLOGY
Summary Report

In Situ Redox Manipulation

OST/TMS ID 15

Subsurface Contaminants Focus Area

Demonstrated at
Hanford Site
Richland, Washington

INNOVATIVE
TECHNOLOGY
Summary Report

Purpose of this document

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine whether a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE’s Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

All published Innovative Technology Summary Reports are available on the OST Web site at http://ost.em.doe.gov under “Publications.”

TABLE OF CONTENTS

APPENDICES

SECTION 1
SUMMARY

Technology Summary

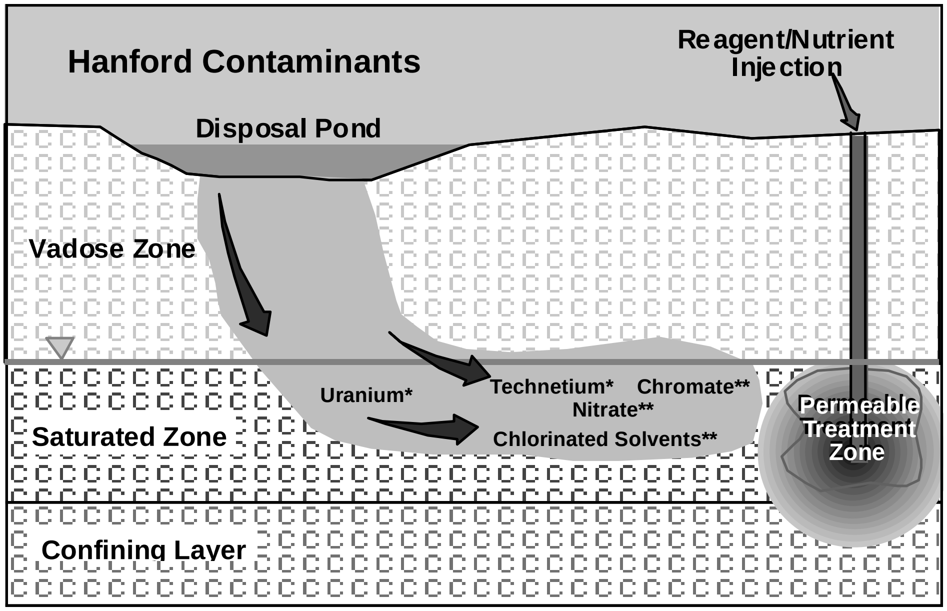
Problem

Operations have contributed contamination to the subsurface at a number of DOE sites. These contaminants have migrated to the groundwater at these sites. Contaminants in the groundwater are often laterally dispersed over large areas and located vertically at depths up to hundreds of feet below the ground surface. Groundwater contaminants are difficult to treat; the baseline techniques of excavation and/or pump and treat are very expensive over the life-cycle of the project, often projected to be in excess of 30-200 years.

How It Works

In Situ Redox Manipulation (ISRM) is a technology based upon the in situ manipulation of natural processes to change the mobility or form of contaminants in the subsurface. ISRM was developed to remediate groundwater that contains chemically reducible metallic and organic contaminants. ISRM creates a permeable treatment zone by injection of chemical reagents and/or microbial nutrients into the subsurface downgradient of the contaminant source. The type of reagent is selected according to its ability to alter the oxidation/reduction state of the groundwater, thereby destroying or immobilizing specific contaminants. Because unconfined aquifers are usually oxidizing environments and many of the contaminants in these aquifers are mobile under oxidizing conditions, appropriate manipulation of the redox potential can result in the immobilization of redox-sensitive inorganic contaminants and the destruction of organic contaminants. This concept requires the presence of natural iron, which can be reduced from its oxidized state in the aquifer sediments to serve as a long-term reducing agent. The figure below depicts the ISRM concept.

Figure 1. ISRM Concept



* Potential Candidate for Redox Treatment
** Favorable Candidate for Redox Treatment

- A chemical reducing agent such as sodium dithionite is injected into the aquifer through a standard groundwater well.
- The reducing agent reacts with iron naturally present in the aquifer sediments in the form of various minerals (clays, oxides, etc.).
- Reaction products from the dithionite (largely sulfate) and any mobilized trace metals are withdrawn from the aquifer and disposed.
- Redox sensitive contaminants that migrate through the reduced zone in the aquifer become immobilized (metals) or destroyed (organic solvents). Potential contaminants for treatment with ISRM include: chromate, uranium, technetium, and chlorinated solvents.
- ISRM is a passive barrier technique, with no pumping or above-ground treatment required once the treatment zone is installed. For this reason, the operation and maintenance costs after installation are very low.

Potential Markets

Potential markets include sites where groundwater contamination (redox-sensitive metals, such as chromium, uranium and technetium, inorganic ions, radionuclides, and chlorinated hydrocarbons) is dispersed over large areas and is deeper than 30 feet below the surface.

Advantages over Baseline

- A permeable treatment zone would be a permanent solution for groundwater remediation.
- The technology is expected to be cheaper than the pump-and- treat baseline because the cost of installation for both options is comparable, but long-term operation and maintenance costs are significantly less with ISRM.
- The treatment zone remains active in the subsurface, where it is available to treat contaminants that seep slowly from less permeable zones.
- ISRM minimizes human exposure to contaminants during remediation because neither contaminated groundwater nor matrix material are brought above ground.
- The barrier is renewable if the original emplacement does not meet performance standards

Demonstration Summary

This report covers demonstrations that took place between September 1995 and September 1998 at the DOE Hanford Site in Washington State. Performance of the technology is based upon the initial “proof of principle” demonstration at the Hanford Site’s 100-H Area in 1995 and the Treatability Test in 1997-1998 at the 100-D Area. The 100 Area of the Hanford Site, the site of nine nuclear reactors, is located in the north-central part of the site near the Columbia River. During reactor operations, chromium was introduced to the soil and, ultimately, the groundwater in this area. Aqueous chromate concentrations in the reduced zones in the 100-H Area were 60 parts per billion (ppb) and 910 ppb in the 100-D Area prior to the ISRM tests. Depth to the uppermost unconfined aquifer at the 100-H area is approximately 50 feet, while it is approximately 85 feet at the 100 D area. The unconfined aquifer is approximately 15-20 feet thick in the 100 Area.

- The initial demonstration was designed as a “Proof of Principle” field test:
    1) to demonstrate that a pilot-scale reduced zone could be created in the Hanford unconfined aquifer;
    2) to demonstrate feasibility of scale-up from laboratory to pilot-scale in-situ conditions;
    3) to design a plan for assessing performance and longevity of a pilot-scale demonstration of the ISRM technology.
- The second test was a treatability field-scale demonstration of ISRM. This demonstration was designed to provide the required cost and performance data for identifying requirements for

constructing a full-scale barrier and to assess ISRM effectiveness for remediating chromium-contaminated groundwater, by treating a 150 foot x 50 foot area.

- A full-scale deployment at the Hanford 100-HR-3 Operable Unit is planned to begin in late ‘99.

Key Results

- Aqueous chromate concentrations within the reduced zone (50 feet in diameter) decreased to below detection limits (<8ppb).
- Two years after the injection of sodium dithionite reducing agent, the treatment zone remains anoxic and chromate remains below detection.
- A cost-benefit analysis showed that ISRM could save 60% of the cost of a pump-and-treat system for remediating groundwater contaminated with chromate at Hanford over a 10-year period.
- Bench-scale tests have demonstrated destruction of trichloroethylene (TCE) and perchloroethylene (PCE) by redox manipulation.
- ISRM has also been demonstrated to treat TCE contamination at a Fort Lewis, Washington DoD site in 1998 and will be demonstrated at DoD’s Moffett Field, California in 2000.

Commercial Availability

- Battelle Pacific Northwest National Laboratory is currently working with commercial partners to deploy the technology.

Contacts

Technical

John Fruchter, Principal Investigator, Pacific Northwest National Laboratory (PNNL), 509-376-3937.
Wayne Martin, Pacific Northwest National Laboratory (PNNL), 509-372-4881

Management

Jim Wright, DOE EM-50, Subsurface Contaminants Focus Area Manager, (803) 725-5608

Other

All published Innovative Technology Summary Reports are available online at http://em-50.em.doe.gov. The Technology Management System, also available through the EM-50 web site, provides information about OST programs, technologies, and problems. The OST reference number for ISRM is 15.

SECTION 2
TECHNOLOGY DESCRIPTION

Overall Process Definition

Process Descriptions

- The ISRM treatment zone is created through a three-phase process:
  - — During the injection phase, a reagent is injected into the aquifer through injection/withdrawal wells at the rate and duration required to treat the desired volume of aquifer sediments. This treatment volume plus the quantity of available iron in the sediments determines the amount of reductive capacity generated in the barrier and, ultimately, the barrier's duration.
  - — During the residence phase (approximately 18 hours), the reagent is allowed to react with the aquifer sediments. The reductant reacts with the iron in the sediments by the following reaction:

$$\mathbf{SO_2^{-} + Fe^{+3} + H_2O = SO_3^{-2} + Fe^{+2} + 2H^{+}}$$

  - — During the withdrawal phase, unreacted reagent, buffers, reaction products, and mobilized trace metals are withdrawn through the injection/withdrawal wells.
- Following creation of the ISRM treatment zone, contaminated groundwater flows through the permeable barrier under natural gradient conditions. No pumping or above-ground treatment is required, greatly decreasing the long-term maintenance and operation cost.
- Target contaminants are destroyed or immobilized by interactions with the reduced structural Fe in the ISRM treatment zone. Chromate is immobilized by reduction to highly insoluble chromium hydroxide or ferric-chromium hydroxide.

$$\mathbf{3Fe^{+2} + CrO_4^{-2} + 5H^{+} = Cr(OH)_3 + 3Fe^{+3} + H_2O}$$

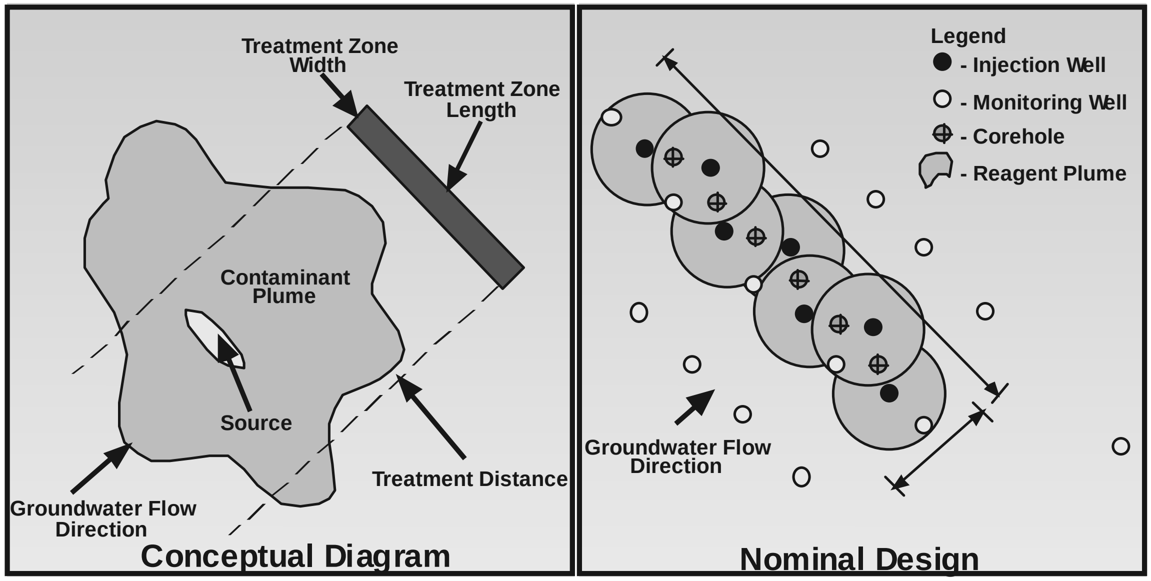
- An ISRM treatment zone removes dissolved oxygen in the migrating groundwater by the very fast reaction:

$$\mathbf{4\,Fe^{+2} + O_2 + 4H^{+} = 4\,Fe^{+3} + 2H_2O}$$

This reaction creates a deoxygenated plume of groundwater within the treatment zone.

- If the original ISRM barrier emplacement does not meet target cleanup levels, the treatment zone's reductive capacity can be restored by repeating the emplacement process. This can be done using existing injection/withdrawal wells, so a large investment is not required.
- The redox altering reagent used in these tests was sodium dithionite ($Na_2S_2O_4$). The dithionite ion, commonly known as hydrosulfite, is a strong reductant, particularly in strongly basic solutions.
- Reduction reactions with the dithionite ion typically proceeds in two steps: dissociation of the dithionite ion to form two sulfoxyl (SO_2^-) radicals; reaction of these radicals with the oxidized species (Fe^{+3}) yields a reduced species (Fe^{+2}) and sulfite (SO_3^{-2}) or bisulfite (HSO_3^-).

A conceptual diagram of the In Situ Redox Manipulation process is shown in the figure below.



Conceptual Diagram and Design of ISRM barrier

System Operation

Operational parameters such as rate of injection, pressure, volume of reagent, and time of injection are determined based upon specific site characteristics and needs, such as hydraulic conductivity of the aquifer, thickness of the aquifer, spacing of injection wells, etc.

Materials and equipment to be used to deploy ISRM include the sodium dithionite reagent and the following equipment: four different types of well, field trailers, mixing and storage tanks, pumps, and analytical equipment. The wells included: five injections/withdrawal wells, four standard monitoring wells, two multilevel monitoring wells, and three Westbay multilevel monitoring wells. Ten 20,000 gallon frac tanks were used to hold groundwater for dilution of concentrated tracer solutions and reagent for treatment zone emplacement. Two pumps were used for the bromide tracer test and dithionite injection/withdrawal test, a 0.75 horsepower pump and a 3 horsepower pump.

Manpower skills and training required include standard drilling operators for installation of the injection and monitoring we3lls, a field operator who is familiar with pumps, valves, piping, and handling of chemicals, and a field analytical chemistry technician.

Secondary waste generated by ISRM includes aqueous potassium/sodium sulfate at a volume of approximately 100,000 gallons per well according to the site-specific conditions required at the Hanford site.

Operational risks and concerns are equivalent to those of a pump and treat operation, but also include concerns regarding handling of chemicals, i.e. the reagent, and injection of fluids as opposed to simple extraction during a pump and treat operation.

SECTION 3
PERFORMANCE

Demonstration Plan

Performance of the technology is based upon the initial "proof-of-principle" demonstration at the Hanford Site's 100-H Area in 1995 and the Treatability Test in 1997-1998 at the 100-D Area. The 100 Area of the Hanford Site, the site of nine nuclear reactors, is located in the north-central part of the site near the Columbia River. During reactor operations, chromium was introduced to the soil and, ultimately, the groundwater in this area.

- Aqueous chromate concentrations in the reduced zones in the 100-H Area were 60 ppb and 910 ppb in the 100-D Area prior to the ISRM tests.
- Depth to the uppermost unconfined aquifer at the 100-H area is approximately 50 feet, while it is approximately 85 feet at the 100 D Area.
- The unconfined aquifer is approximately 15-20 feet thick in the 100 Area.

The objectives of the two demonstrations, one in the 100-H Area and one in the 100-D Area, were to:

- Establish feasibility of creating a reduced zone in the aquifer using ISRM, and the possibility of scaling up to full scale during both tests.
- Evaluate secondary effects of the process.
- Develop a strategy for a pilot test-scale deployment of ISRM at Hanford during the proof of principle test in 1995. The pilot test was performed in 1997 and 1998.

During the "proof-of-principle" test in the 100-H Area, operations included the following:

- 77,000 liters (20,500 gallons) of buffered sodium dithionite solution were successfully injected into the unconfined aquifer through a single 8-inch diameter injection/withdrawal well, creating a reduced zone approximately 15 m (50 ft) in diameter.
- The sodium dithionate reagent was allowed to react with the aquifer sediments for approximately 18 hours, and then was withdrawn. The buffer solution consisted of potassium carbonate/potassium bicarbonate at pH 11. The potassium salts also prevent dispersion of clays. During the withdrawal phase (83 hours, 4.8 injection volumes), unreacted reagent, buffer, reaction products, bromide tracer, and mobilized metals were withdrawn through the same well.
- Sixteen 2-inch-diameter monitoring wells were placed at various radial distances to assess physical and chemical conditions after the test. The monitoring wells were screened in either an upper or lower zone and they were located up and downgradient of the injection/extraction well. The site was characterized by a number of methods including hydraulic tests and a bromide tracer test to determine hydrology, geology, geochemistry and microbiology. Dithionite migration and reactivity were characterized by monitoring DO, pH, and electrical conductivity in groundwater and by directly measuring dithionite in the groundwater withdrawn from the injection well.

Results

- ISRM is able to reduce aqueous concentrations of chromate in the groundwater to less than 8 ppb in one month, versus many years of operation for a pump and treat system. The performance of ISRM is thus enhanced over that of the baseline in terms of time required to reach cleanup goals.

- Between 87% and 90% of the dithionite solution was recovered during the withdrawal phase, and most of the mobilized trace metals (Fe, Mn, Zn) were removed during this phase.
- A thin zone (1 to 4 inches) of reduced permeability occurred near the injection/withdrawal well, but this resulted in no significant adverse effects on performance.
- Within a 25-foot radial distance of the injection well, core analyses showed that 60% to 100% of the available reactive iron was reduced; this emplacement zone is estimated to have a life of 7 to 13 years, based on post-test core data.
- Two years after treatment at the 100-H Area, the treatment zone remains anoxic and hexavalent chromium remains below detection.
- Initial total chromium concentrations (as chromate) within the treatment zone ranged from 46 to 71 ppb; following the ISRM test, total chromium concentrations were near the detection limit (2 ppb).
- Other trace metals, such as arsenic and lead, mobilized by the reductant, remain below maximum allowable drinking water concentrations.

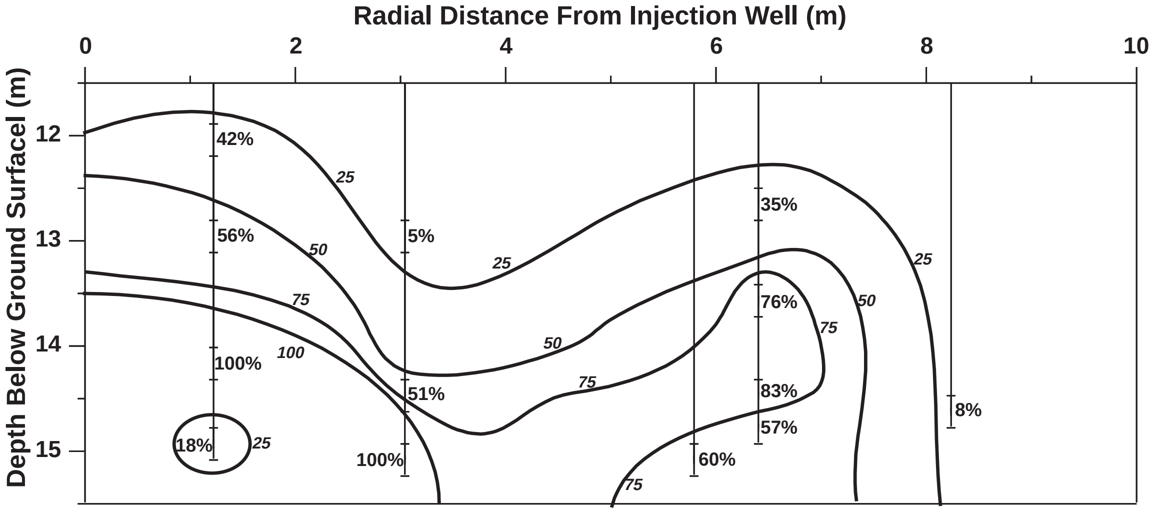


Figure 3. Contour Plot of Available Reduced Iron (%)

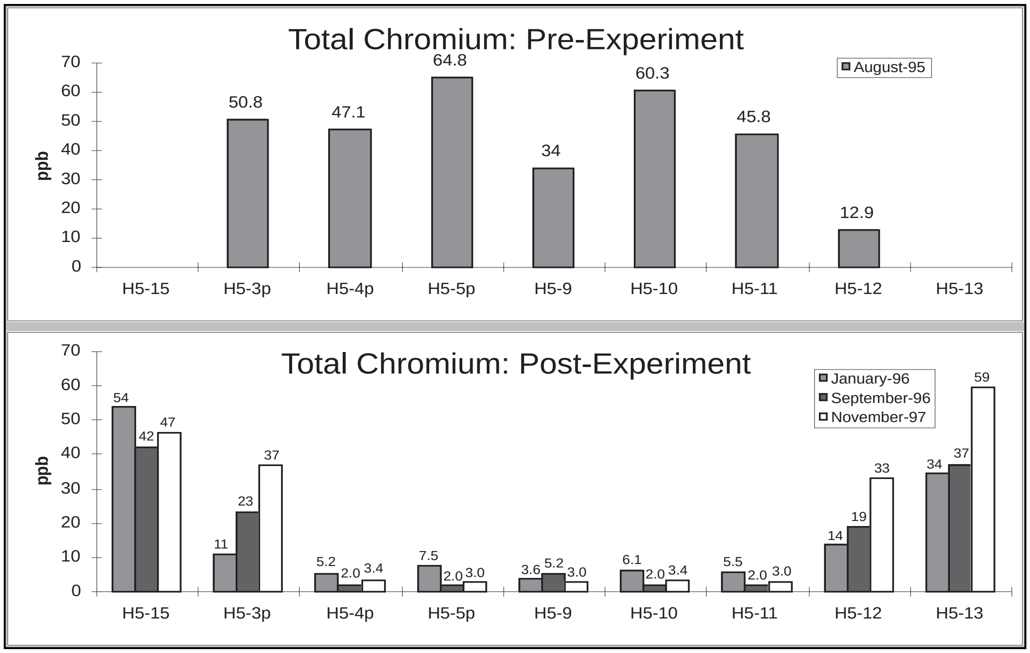


Figure 4. Total Chromium by Well Over Time

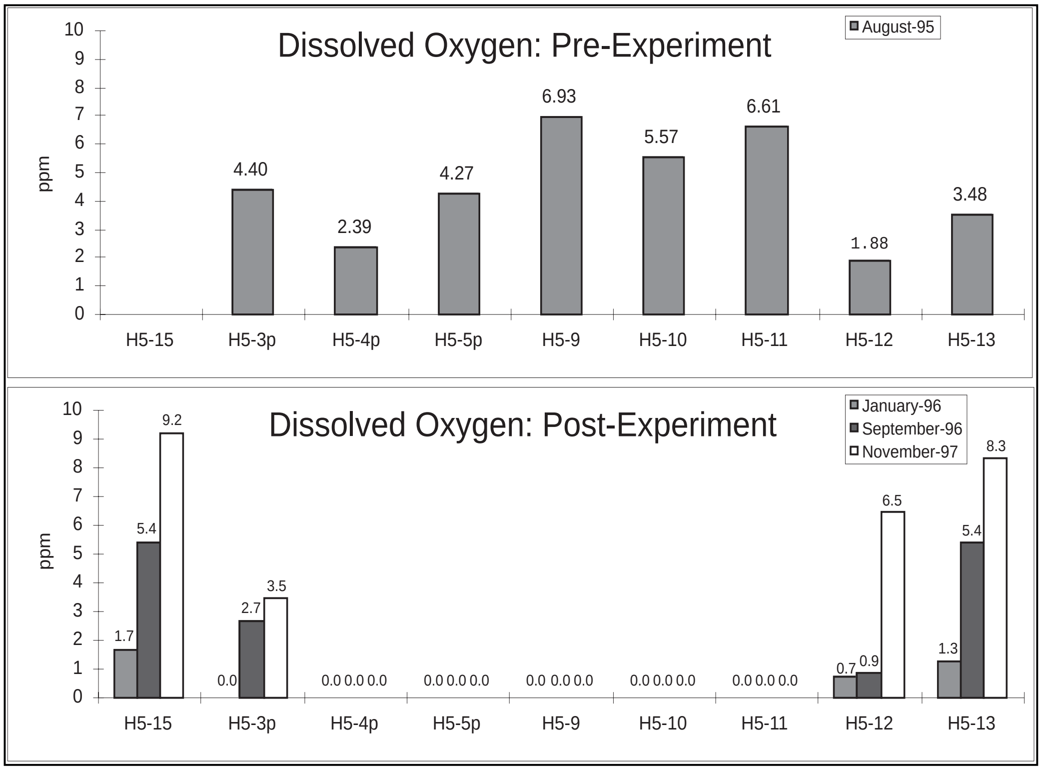


Figure 5. Dissolved Oxygen by Well Over Time

SECTION 4
TECHNOLOGY APPLICABILITY AND ALTERNATIVES

Competing Technologies

- The baseline against which ISRM can be compared is pump and treat. Pump and treat technology generally requires long treatment times and has high operation and maintenance requirements and costs.
- Another competing technology is the permeable reactive treatment barrier. Because ISRM technology is deployed through groundwater wells, it can be used at greater depths than conventional trench-and-fill reactive barriers which are best suited for applications less than 40 feet below the ground surface.
- For organic contaminants, other competing technologies include in well vapor stripping, air sparging, and bioremediation.

Technology Applicability

- ISRM has been demonstrated in field tests to reduce chromate concentrations in groundwater to near detection levels (2 ppb). Hexavalent chromium is reduced to the +3 state, which is not easily reoxidized.
- Bench-scale tests have shown that ISRM is also effective for treatment of dissolved trichloroethylene (TCE) and uranium in groundwater. Bench-scale or lab-scale tests are currently planned using soils from DOD sites in California and Washington State to determine applicability.
- ISRM is well suited for sand or sand and gravel aquifers, which have sufficient hydraulic conductivity to allow injection and significant migration of dithionite solution before it reacts to form sulfate, thiosulfate, and sulfite. Low permeability aquifers are not suited for ISRM.

Patents/Commercialization/Sponsor

- One patent, number 5,783,088, was issued to Battelle Pacific Northwest National Laboratory on July 21, 1998.
- Battelle Pacific Northwest National Laboratory, is currently seeking commercial partners to deploy the technology.

SECTION 5
COST

Cost Methodology

Information in this preliminary cost analysis was prepared from data provided by PNNL to Los Alamos National Laboratory (LANL), which performs independent cost analyses for the Office of Science and Technology (OST).

- The pump-and-treat technology was the baseline against which ISRM was compared.
- To develop the cost analysis comparison, the following scenario was used:

  - The objective is to prevent the migration of hexavalent chromium through a section of aquifer 200 feet long, similar to the treatment cell size used during the 1997-1998 field-scale demonstration.
  - The ISRM design requires drilling 3 coreholes, 7 injection/withdrawal wells, 4 compliance monitoring wells, and 1 performance monitoring well across the 200 foot section of aquifer to prevent the downgradient migration of chromium. The barrier width, in the direction of groundwater flow, is approximately 50 feet. Emplacement of the ISRM permeable barrier and required residence time in the aquifer to initiate conditions for the redox reactions may take only several days, but the lifetime of the treatment barrier is expected to be at least 10 years.
  - The baseline technology is a typical pump-and-treat system designed to target hexavalent chromium at a DOE site. A 200-foot section of aquifer is assumed to require a single extraction well and a single injection well. To simplify the comparison, it is assumed that compliance and performance monitoring wells are equivalent for each technology. Using a 25 gallon per minute (gpm) extraction rate, the single extraction well processes approximately 13 million gallons of groundwater per year after it is fully operational. Treated groundwater is reinjected upstream of the contaminated plume after processing by the ion exchange plant. The pump-and-treat plant is assumed to have a design life of 10 years under normal operation and maintenance conditions and to operate continuously.
  - For both technologies, the scenario assumes a 10-year project life. The scenario assumes design, construction, procurement, and construction costs occur in the first year and that both technologies become operational in the second year.
  - The scenario requires chromium to be removed to the maximum extent practicable with concentrations not to exceed 50 ppb in the pump-and-treat discharge or the monitoring samples for ISRM. The goal of the scenario is only containment of the plume, not remediation.

A more recent cost analysis comparing the full-scale (1400-ft long barrier) deployment of ISRM at Hanford to that of a planned pump and treat system was published in Soil and Groundwater Cleanup, October 1998.

- This comparison assumes the pump and treat system and the ISRM barrier operate until 2030. However, the pump and treat actually operates for only 5 years and is then followed by a monitoring program through 2030. The ISRM barrier assumed are-injection of dithionite in 2015.

Cost Analysis

The following table includes the results of the LANL analysis.

Cost Conclusions

The full-scale cost comparison (Soil and Groundwater Cleanup, 1998) shows the cost of the pump and treat system to range between $21 and $29 million, depending on the discount rate. The ISRM barrier costs range from $9 to $13 million. This amounts to projected cost savings of $12 to $16 million.

- Estimated cost savings over pump and treat are $4.6 million, a savings of 60% over a ten-year period using the LANL analysis described at the beginning of Section 5. Using the Soil and Groundwater Cleanup analysis, cost savings are estimated at $12-16 million if applied at the Hanford Site

SECTION 6
REGULATORY AND POLICY ISSUES

Regulatory Considerations

- Under CERCLA, onsite treatability tests may be conducted without any federal, state, or local permits. Thus, no specific permits were required for the field test at Hanford. Regulatory approval was given after a “mini” dithionite injection was conducted.
- Future application of ISRM may require underground injection permits and NEPA review.
- Under CERCLA, the major ARARs pertinent to this technology are groundwater standards, Columbia River Protection Standards, cultural and ecological resource protection requirements, and water and wastewater management standards.
- Some state agencies are concerned about injection of fluids and materials that may alter the pH of the subsurface.

Safety, Risks, Benefits, and Community Reaction

Worker Safety

- Health and safety issues for the ISRM technology does not present significant hazards over conventional field remediation operations.
- Reagents used in the process are easily managed using standard chemical handling procedures.

Community Safety

- ISRM does not produce any routine release of contaminants.
- No unusual or significant safety concerns are associated with the transport of equipment, samples, waste, or other materials associated with ISRM.
- Careful monitoring of field operations assures safety to workers and the public.

Environmental Impacts

- No additional impacts will be produced over those already anticipated as a result of site remediation.

Socioeconomic Impacts and Community Perception

- ISRM has a minimal economic or labor force impact.
- The general public has limited familiarity with this technology.

SECTION 7
LESSONS LEARNED

Design Issues

- The ability of the dithionite solution to penetrate far enough into the aquifer to create a continuous barrier depends on both the hydraulic conductivity of the aquifer and the iron content of the aquifer sediments. If the iron content is too low, insufficient reducing capacity will be available. If the amount of reactable iron is too high, the dithionite will be consumed before it travels far enough into the aquifer to provide reasonable coverage. therefore, accurate measurements of both of these parameters and design analysis incorporating them are crucial to the success of the project.

Implementation Considerations

- During early phases of the implementation at the first field site, oxygen was introduced into the reduced zone through the monitoring wells. This problem was corrected by blanketing the monitoring well with argon.
- To keep oxygen out of the dithionite mixing tanks, the headspaces were also blanketed with argon. At first, nitrogen was sparged through the solution, but there was sufficient oxygen as a contaminant in the nitrogen to cause problems, so this method was abandoned. In later tests, the dithionite was diluted as it was injected, so that mixing tanks were not used.

Technology Limitation/Need for Future Development

- Longer-term performance data are required to assess the need for design improvements and system optimization. This information can then be used to better quantify life-cycle costs.
- Optimization of injection concentrations, rates, and geometries should be addressed in future applications.

APPENDIX A
REFERENCES

Cummings, M. A. and S.R. Booth. 1997. Cost-Effectiveness of In Situ Redox Manipulation for Remediation of Chromium-Contaminated Groundwater. LA-UR-97-165, Los Alamos National Laboratory, Los Alamos, New Mexico.

Williams, M. D. et al, 1998,. 100-D Area In Situ Redox Treatability Test for Chromate-Contaminated Groundwater FY 1998 Year-End Report. Pacific Northwest National Laboratory, Richland, Washington.

Scott, M. J., F. B. Metting, J. S. Fruchter, and R. E. Wildung, 1998, Research Investment Pays Off, Soil and Groundwater Cleanup, October 1998, p. 6-13.