

**In Situ Redox Manipulation for Immobilization of Inorganic
Contaminants: Subsurface Barrier Technology Results in
Significant Cost Savings, Demonstrating the Value of Basic
Science Investments**

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The U.S. Department of Energy (DOE) is landlord for the nation's nuclear defense complex, which includes numerous waste sites, many of which harbor complex mixtures of metals and radionuclides, often with halogenated and other organic contaminants. DOE is responsible for more than 130 installations totaling approximately 7280 km² in 30 states and territories with collectively more than 2500 billion liters of contaminated groundwater and 200 million m³ of contaminated soils and sediments. It has been estimated that managing DOE's legacy wastes and restoring contaminated subsurface environments across the nuclear weapons complex will entail a decades-long effort costing many tens of billions of dollars (DOE 1995).

Realizing the scope of the problem led DOE to create the Subsurface Science Program (SSP) in its Office of Energy Research. Nearly 10 years of cross-disciplinary, multi-institutional research has significantly advanced our understanding of complex and interactive geochemical, microbiological, and physical processes and resulted in novel concepts for soil and groundwater cleanup. One example of a "spin-off" technology that can be directly traced to advances in basic science is a process for *in situ* reduction-oxidation manipulation (ISRM). ISRM treats reduction-oxidation (redox)-sensitive contaminants in unconfined aquifers by injecting chemical reagents into the subsurface to chemically or biologically create a permeable reducing zone (or barrier) that intercepts contaminants moving in a groundwater plume. Important inorganic contaminants that are mobile under oxidizing conditions are immobilized by changing the redox status of the subsurface. This can be effective for metals and radionuclides such as chromium (Cr), uranium (U), and technetium (Tc).

Recently, a successful field demonstration of ISRM at DOE's Hanford Site in southeastern Washington State showed how, in select cases, basic research can be linked directly to technology innovation with the potential for significant cost savings.

In Situ Redox Manipulation

Companies and government agencies responsible for contaminated sites are limited in their choice of effective, inexpensive cleanup methods. The baseline technology for groundwater restoration is removal and above-ground treatment known as "pump-and-treat." This approach is now generally recognized as costly and largely ineffective, in part because of the decades-long treatment times that are often required (National Research Council 1994; 1997). A number of

promising concepts for *in situ* treatment to replace or augment pump-and-treat are being evaluated. These include different subsurface treatment zones, which typically consist of down-gradient trenches backfilled with one or more reactive materials selected to promote a particular treatment process. “Trench-and-fill” methods, however, become impractical deeper than about 40 feet below ground surface. Therefore, investigations have been directed toward creating permeable barriers at depth. Many deep aquifers are oxidizing environments in which contaminants such as Cr, U, and Tc are mobile in the oxidized state. Also, many aquifers thought to be reducing are nevertheless sufficiently oxidized due to recharge with oxygenated water to maintain contaminant mobility. If the redox potential of the aquifer can be made reducing, then a variety of inorganic contaminants can be treated. Reducing conditions can also favor dehalogenation of organic contaminants, such as trichloroethylene (TCE) and carbon tetrachloride (CCl₄) (Amonette et al. 1994; Fruchter et al. 1994; 1996; Vermeul et al. 1995).

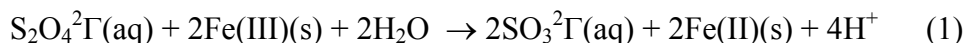
The aim of ISRM is the creation of a long-lived permeable treatment zone in the subsurface (Figure 1). The treatment zone is created by reducing structural ferric iron to ferrous iron within the minerals of the aquifer sediments (Figure 2), which in turn serve as a long-term, solid-phase reducing agent. This is accomplished by introduction of chemical reducing agents such as sodium dithionite. After the aquifer sediments are reduced, excess reagent and soluble reaction products are removed from the subsurface. Redox-sensitive contaminants that pass through the zone are reduced and immobilized as solids. Chromate, for example, is immobilized by reduction to highly insoluble chromium hydroxide or iron chromium hydroxide. This is particularly favorable because Cr is not easily resolubilized as groundwater flow gradually reoxidizes the environment with time. Uranium and Tc can also be reduced to less soluble forms, but their long-term stability to reoxidation has not been fully tested in the field.

[Figure 1 about here – conceptual model of ISRM -- plume scale]

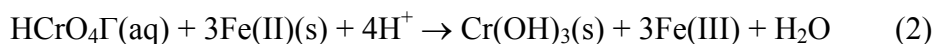
[Figure 2 about here – conceptual pore scale model]

Field Demonstration

Injecting a solution of dithionite into a series of wells located downgradient of a contaminant plume at Hanford was originally proposed to test ISRM in the field (Amonette et al. 1994). Within the aquifer, the injected dithionite reacts with structural iron in layered silicates and on the surface of oxyhydroxide minerals, reducing Fe(III) to Fe(II) according to the overall reaction:



Within the zone of dithionite-treated sediments, aqueous chromate reacts with Fe(II) produced by the dithionite reaction (Eq. 1) and is precipitated as a solid hydroxide (e.g., Cr(OH)₃) according to Eq. 2:



Dithionite is unstable in aqueous solution at neutral and acidic pH and can undergo disproportionation reaction that can lower dithionite concentrations and the ultimate quantity of

Fe(II) produced. Because its stability is greatly enhanced at high pH, dithionite in a potassium carbonate/potassium bicarbonate buffer at pH 11 was used successfully to demonstrate the reduction of iron-bearing minerals in Hanford Formation sediments and the subsequent removal of Cr(VI) from groundwater. The potassium salts in the buffer are used to prevent dispersion of the clays and loss of the barrier once the groundwater returns to its original ionic strength. A CO_3/HCO_3 buffer is used rather than a $\text{HCO}_3/\text{CO}_2(\text{g})$ buffer to minimize CO_2 gas production that would affect aquifer permeability.

The pilot-scale dithionite injection experiment was initiated in September 1995 at Hanford's 100-H Area, southwest of a retired plutonium production reactor and about 730 m from the Columbia River (see accompanying photo). This site was chosen because hexavalent Cr is present at about 70 ppb, below the 100 ppb regulatory limit for groundwater but still sufficient to demonstrate the technology. Sixteen wells were drilled and completed, including an injection/withdrawal well, upper- and lower-zone monitoring wells, and up- and down-gradient monitoring wells. Prior to the full-scale injection, a series of site-characterization activities were completed, including hydraulic tests and a bromide tracer test. The experiment was designed to produce a 15-meter diameter reduced zone. Buffered sodium dithionite solution (20,500 gal) was injected into the aquifer over 17 hours. After an additional reaction time of 18.5 hours, the spent reagent was withdrawn from the aquifer over the next 83 hours, representing 4.8 injection volumes. The withdrawal task was designed to remove unreacted reagent and buffer, reaction products (e.g., sulfate/sulfite), mobilized metals, and residual bromide tracer. Analysis indicated that ninety percent of the injected dithionite was withdrawn as sulfate or sulfite.

[Photo about here—Hanford ISRM Test Site, 100 Area]

Data on cores taken after the injection showed that 60% to 100% of the available reactive iron in the sediments was reduced by the dithionite, depending on location within the treatment zone. This translated to levels of reducing capacity between 51 and 85 pore volumes, or 7 to 12 years for groundwater with 1-ppm hexavalent chromium and 9-ppm dissolved oxygen. Two years after the injection, groundwater in the injection zone remains anoxic. Hexavalent chromium levels remain below detection limits, while total chromium remains in the 1-ppb to 4-ppb range. Other trace metals (e.g., arsenic, lead) mobilized into the groundwater during the reduction phase remain below maximum allowable drinking water concentrations. Concentrations of constituents in the water withdrawn for the test well met all applicable Hanford purgewater criteria and the water was disposed to the ground.

This “proof-of-principle” test conducted at the 100-H Area demonstrated that:

- sediments in the aquifer were successfully reduced by treatment with a chemical reducing agent,
- reduced sediments substantially lowered the concentration of dissolved hexavalent chromium in the groundwater, and
- reducing conditions can be maintained in the aquifer for extended periods of time.

Recently, the technology received a U.S. patent (Amonette et al. 1998).

Cost Savings from ISRM

To calculate the savings associated with the basic research investment in ISRM, costs associated with a hypothetical commercial application were estimated, with the research costs associated with the development of the concept subsequently subtracted. Estimates compare the full-scale 1500-ft ISRM barrier (formed with overlapping injection/withdrawal systems) with the baseline pump-and-treat system previously planned for treating a Cr plume at Hanford. For purposes of this comparison, the baseline pump-and-treat system and the ISRM barrier system are both assumed to operate until the year 2030. The baseline program is assumed to involve five years of pump-and-treat, followed by a monitoring program through 2030. Because the baseline system, although well understood in principle, has not been applied to the Cr problem at Hanford, its costs are assumed to be subject to $\pm 20\%$ uncertainty. Because of its novelty, the cost of the ISRM barrier was assumed to be even more uncertain: $\pm 50\%$ is used.

Depending on the discount rate, the expected present value of the costs of conventional pump-and-treat technology was estimated at between \$21 million and \$29 million (Table 1)¹. A significant issue is whether 5 years of treatment will be sufficient. For example, if cleanup is incomplete and the baseline system needs to be active an additional 5 years beyond 2003, costs would increase to between \$29 million and \$35 million.

[Table 1 about here]

Costs are estimated at between \$9 million and \$13 million for a full-scale ISRM barrier in place of the pump-and-treat system (Table 2). To develop this estimate, the individual components of the test operation at Hanford were scaled up for barrier size and adjusted for the operational differences between commercial and demonstration-scale units. The barrier was assumed to operate until the year 2030, with a renewal (new injection of dithionite reagent) required in the year 2015. Unlike the pump-and-treat system, which requires substantial operations costs to be effective, ISRM barriers can be left in place and are renewable. Unaccounted for is any additional value associated with the fact that because the barriers are unobtrusive and in the ground, human exposure to contaminants and use of operating machinery is minimal.

[Table 2 about here]

The expected savings associated with the application of ISRM technology at Hanford are shown in the first line of Table 3. To obtain the economic benefit associated with the basic science and subsequent research and development of the technology, we subtracted the costs in the second line of the table. The difference, line 3, is a very conservative estimate of the benefits of the basic scientific research because it assigns all research and development costs to this single application of the technology, even though the technology has a wide variety of potential applications at numerous sites across the country. Even with this conservative estimate, the internal rate of return on the subsurface science investment is about 31% per year. Independent calculations comparing ISRM and pump-and-treat for chromate remediation at Hanford showed a 62% savings over a 10-year period (Cummings and Booth 1997).

¹ All costs shown in the analysis are in constant 1997 dollars. Likewise, the discount rates used in the analysis are real discount rates: that is, they account for the time value of money after any inflation has already been removed.

[Table 3 about here]

To fully understand the contribution made by basic science to this technology, it is desirable also to estimate the value of additional applications of the knowledge. For example, it is anticipated that ISRM will have many applications beyond the Hanford Site. Line 4 of Table 3 provides some rough estimates of the potential cost savings associated with use at an additional 146 sites on the EPA National Priorities List with susceptible inorganic contaminants. These sites represent an average 150,000 m³ of water per site. Pump-and-treat costs range from \$10 to \$100 per cubic meter treated. Based on the Hanford case, average cost savings of up to 30% are possible with ISRM. An estimate of expected savings of \$2.40 per cubic meter at a 5% discount rate was used in line 4 of Table 3.² Total potential net benefits range between \$50 million and \$73 million.

Basic Research and Technology Commercialization

Figure 3 outlines the key steps in the proposed selection and development of new, cost-efficient cleanup technologies by the DOE Office of Environmental Restoration and Waste Management (DOE-EM; DOE 1997). Technology development goes through a series of “gates” in this process, where each gate presents requirements to be satisfied by the technology. Depending on how the technology performs at each gate, it may be forwarded for further development, returned for further assessment, or stopped in its development. The ISRM concept originated from basic research in the DOE Office of Biological and Environmental Research (OBER) and progressed to the demonstration stage (Stage 6). Gate 5 leading to Stage 6 requires that a DOE-EM deployment schedule be established based on documented test results and that the project meet gate programmatic driver criteria that include technology end-user needs; technology merit; costs; safety; health, environmental protection, and risk; and stakeholder, regulator, tribal, and commercial viability. Thus, the ISRM is a classic example of idea generation that leads to a viable product meeting a compelling environmental need.

Clearly, however, there is a complex, non-linear relationship between basic research and the final deployment of technology in the commercial world. The path from basic research to ultimate application is long and seldom straightforward; it can have beneficial impacts in areas of knowledge that can be completely unrelated to the original problem. The main path in the process begins with directed research focused on some problems--in this case, understanding the nature of subsurface environmental contamination, which at its most basic level involves understanding coupled biological, geochemical, and hydrologic processes across temporal and spatial scales. In this case, directed research led to better basic understanding of the redox chemistry of chromium in iron-rich subsurface environments. The discovery of new basic knowledge can, in turn, lead to more applied research—for example, research into how the redox processes might be manipulated *in situ* to influence chromium behavior in groundwater.

[Figure 3 about here]

² The expected value was derived by calculating the average percentage savings from 100 random pairings of the present values of total costs under the pump-and-treat ISRM regimes for the Hanford case. These savings were then applied to the range of costs per unit of \$10 to \$100 per m³.

There may be information feedback to the basic science, as well. Technology innovation and development spans the scale from concept through the lab bench up to prototype demonstration. Technology development often spins out its own research agenda (e.g., the need for a new pumping technology), as well as suggesting applications in unrelated fields. These spillover effects often mean that the total value of a successful innovation is often many times the cost savings associated with how and where the innovation is initially applied, but these additional benefits are often difficult to identify.

Once a technology or innovation has been successfully demonstrated, it can then be deployed and commercialized. The cost savings or sales associated with final application of newly developed products usually provide the basis for economic evaluation of the original research investment. The economic impacts realized from research development include increases in productivity in the federal sector or private sector; changes in economic growth rates; and increases in value or decreases in costs (including environmental costs) of goods and services provided by private and public entities (Averch 1994). The most successful measurements of the value of research are those for which the line from original research to final application is more or less direct and the contribution is both clear and limited in scope. The ISRM approach provides clear economic savings in the treatment of certain groundwater contamination problems, which are also clearly related to the U.S. Department of Energy's Subsurface Science and Technology Development Program.

Acknowledgments

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Table 1. Estimated Costs of Baseline Pump-and-Treat System for Chromium Plume, Hanford Site in Selected Years

Cost Component	Millions of constant 1997 dollars						
	1997	1998	1999	2000	2001	2002	2003-2030
Monitor and sample	\$0.4	\$0.4	\$0.4	\$0.4	\$0.4	\$0.4	\$0.4
Project construction and operations	\$1.6	\$2.3	\$2.4	\$2.4	\$2.4	\$2.4	\$0
Architect/Engineering support	\$0.3	\$0	\$0	\$0	\$0	\$0	\$0
Project support costs	\$1.0	\$0.6	\$0.6	\$0.6	\$0.6	\$0.6	\$0.05
Studies	\$0.1	\$0	\$0	\$0	\$0	\$0	\$0
Expected total	\$3.4	\$3.3	\$3.4	\$3.4	\$3.4	\$3.4	\$0.5
Expected present Value	2% Discount Rate		5% Discount Rate			7% Discount Rate	
	\$28.6		\$23.7			\$21.5	

Table 2. Estimated Costs of ISRM Barrier for Chromium Plume, Hanford Site in Selected Years

Cost Component	Millions of constant 1997 dollars						
	1997	1998	1999	2000	2001	2002	2003-2030
Pre-design characterization	\$0	\$0	\$0	\$0.2	\$0	\$0	\$0
Test planning and design	\$0	\$0	\$0	\$0.2	\$0.08	\$0	\$0
Procurement	\$0	\$0	\$0	\$0	\$2.4	\$0	\$0
Construction	\$0	\$0	\$0	\$3.3	\$0.9	\$0	\$0
Barrier emplacement	\$0	\$0	\$0	\$0	\$2.0	\$0	\$0
Performance monitoring	\$0	\$0	\$0	\$0	\$0.08	\$0.08	\$0.08
Data analysis and test report	\$0	\$0	\$0	\$0	\$0.1	\$0.05	\$0.05
Project management	\$0	\$0	\$0	\$0.104	\$0.1	\$0.02	\$0.02
Total expected value	\$0	\$0	\$0	\$3.7	\$4.8	\$0.15	\$0.15
Expected present value	2% Discount Rate		5% Discount Rate		7% Discount Rate		
	\$12.8		\$10.1		\$8.9		

Table 3. Net Economic Benefits of Subsurface Science Applied to ISRM Technology

Component	Scenario, millions of constant 1997 dollars		
	At 2% Discount Rate	At 5% Discount Rate	At 7% Discount Rate
Cost savings at the Hanford Site	\$15.8	\$13.6	\$12.7
R&D investment	\$6.6	\$6.5	\$6.5
Net benefits	\$9.2	\$7.1	\$6.2
Benefits from other applications	\$63.6	\$52.6	\$47.3
Total net benefits	\$72.8	\$59.7	\$53.5

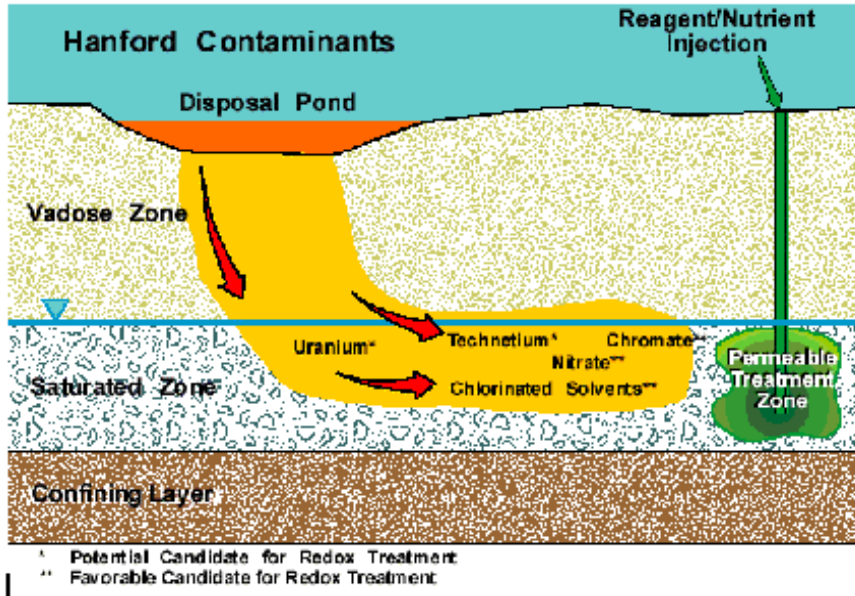


Figure 1. Permeable Geochemical Barrier Approach

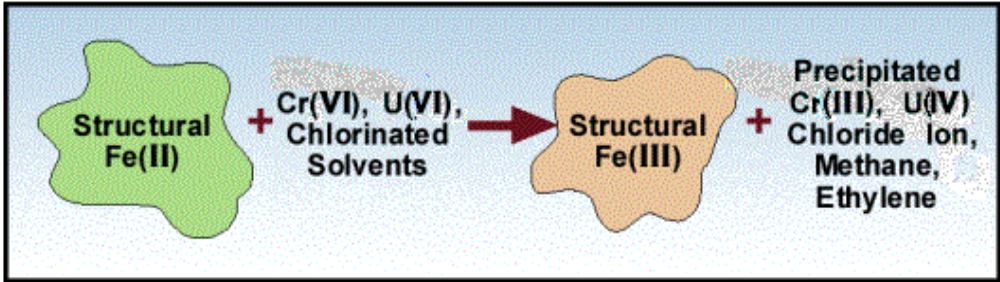
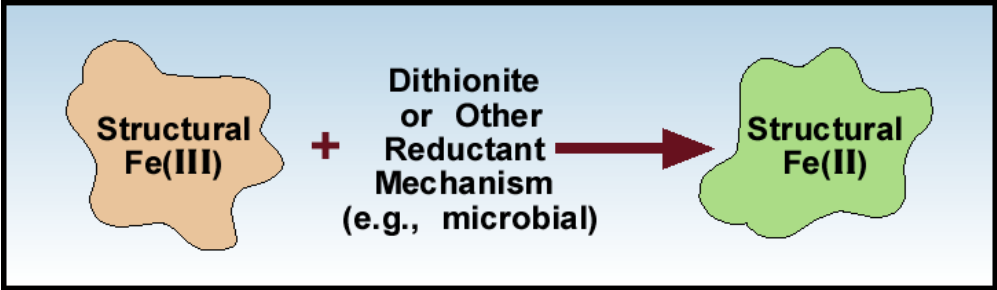


Figure 2. Concept of ISRM Chemistry

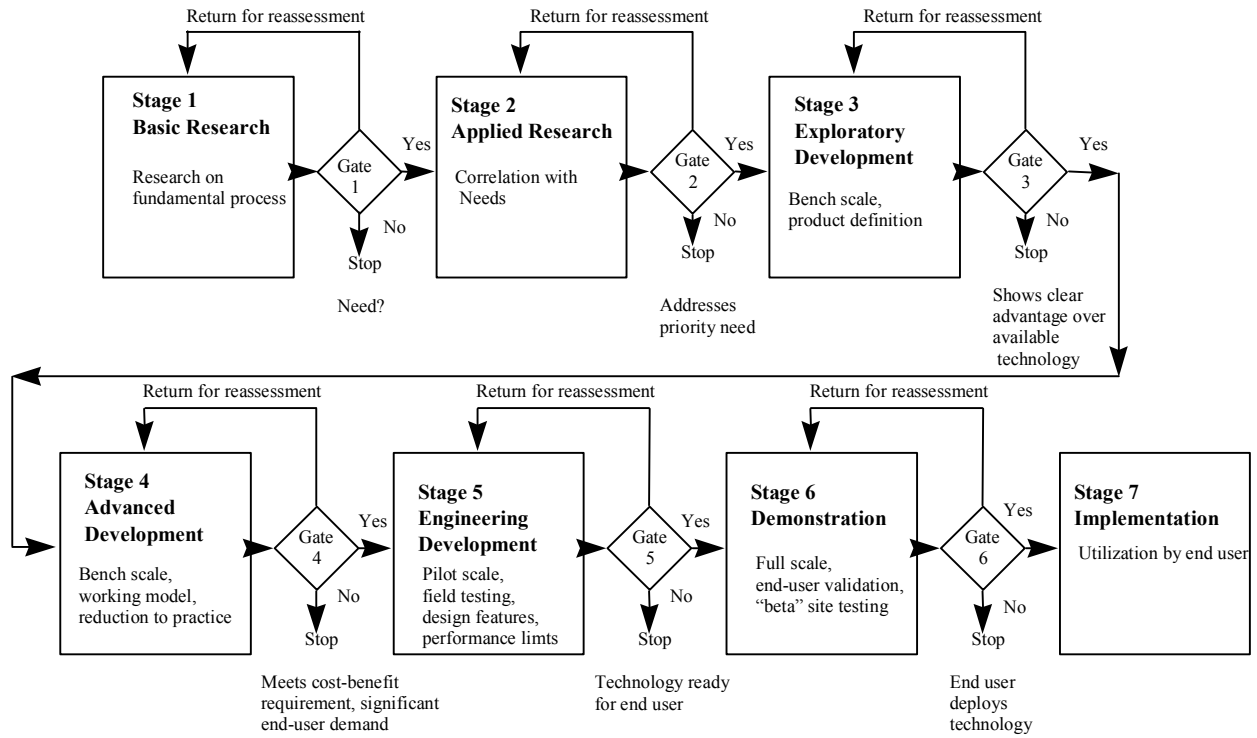


Figure 3. Technology Decision Process