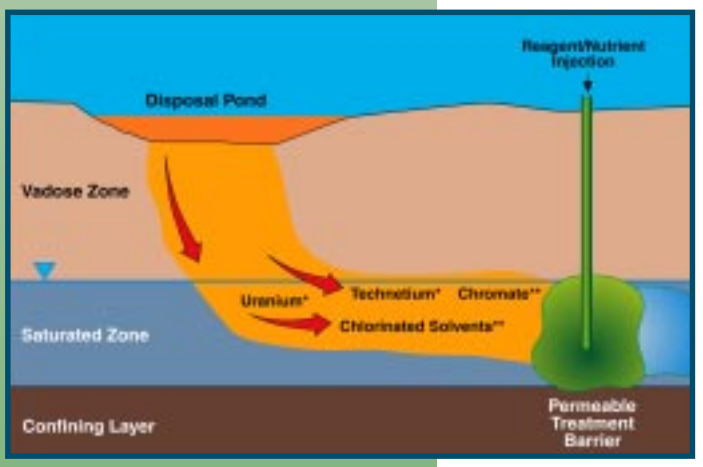
RESOURCE & ECOSYSTEM MANAGEMENT

A Technical Resource for Government and Private Industry

Innovations for Groundwater Cleanup

In Situ Redox Manipulation

In Situ Redox Manipulation is a time- and cost-saving alternative to conventional techniques for cleaning up groundwater contamination. Developed at the Pacific Northwest National Laboratory, ISRM is based on creating a permeable reactive barrier within an aquifer to immobilize or destroy contaminants in the groundwater. Reagents and buffers are injected into the aquifer, reducing the valence state of naturally occurring iron in sediments where the plume flows. The treatment zone is emplaced using conventional monitoring wells; and a series of treatment zones can be coalesced to form a large-scale permeable barrier. The technology is effective for difficult-to-treat problems, such as sites with deep contamination or large dispersed plumes.



ISRM places optimal treatment capacity in the most permeable regions of the subsurface, where contaminant-laden groundwater flows. The technology is economical because, once installed, it does not require ongoing operation and maintenance. Also, ISRM barriers can be placed at greater depths than "trench and fill" permeable reactive barriers, since they are installed through conventional wells.

To form a treatment zone, sodium dithionite (along with pH buffers) is injected through a well and allowed to react for one to two days. Water containing the reaction byproducts and any remaining reagent is pumped out, tested for hazardous constituents, and disposed. The contaminated groundwater flows naturally through the treatment zone where the contaminants react with the reduced iron sediment (not the reagent).

Sodium dithionite ($Na_2S_2O_4$) is a bleach widely used in the paper industry. The dithionite ion dissociates easily into sulfoxyl radicals ($SO_2^{\cdot -}$). Sulfoxyl radicals are strong and highly reactive reductants. These reductants react with the natural iron in the sediments as follows:

$$SO_2^{\cdot -} + Fe(III) + H_2O \Leftrightarrow SO_3^{2-} + Fe(II) + 2H^+$$

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Target contaminants are destroyed or immobilized by interactions with the reduced structural Fe(II) in the ISRM redox zone.

For chromium contamination, the Fe(II) in the sediments causes the dissolved Cr(VI) phase of chromium (CrO_4^{2-}) to precipitate as $Cr(OH)_3$. The reaction is as follows:

$$3\ Fe(II) + CrO_4^{2-} + 3e^- + 5H^+ \Leftrightarrow Cr(OH)_{3(s)} + 3\ Fe(III) + H_2O.$$

For trichloroethylene (TCE) contamination, the TCE is reductively dechlorinated to ethylene as follows:

$$6\ Fe(II) + C_2HCl_3 + 6e^- + 3H^+ \Leftrightarrow C_2H_4 + 6\ Fe(III) + Cl^-.$$

ISRM barriers are designed to be maintenance-free for decades. Barrier longevity or treatment capacity is expressed in terms of the number of pore volumes of groundwater that pass through a unit volume of treated aquifer sediments before contaminants break through at levels above those of regulatory concern.

Treatment capacity is measured in laboratory column tests and provides an estimate of the service life of the redox barrier under ambient groundwater flow rate and site chemistry conditions. Typical lifetimes at sites tested to date are estimated in the 15- to 25-year range.

The patented ISRM technology has received an R&D 100 Award from R&D Magazine.

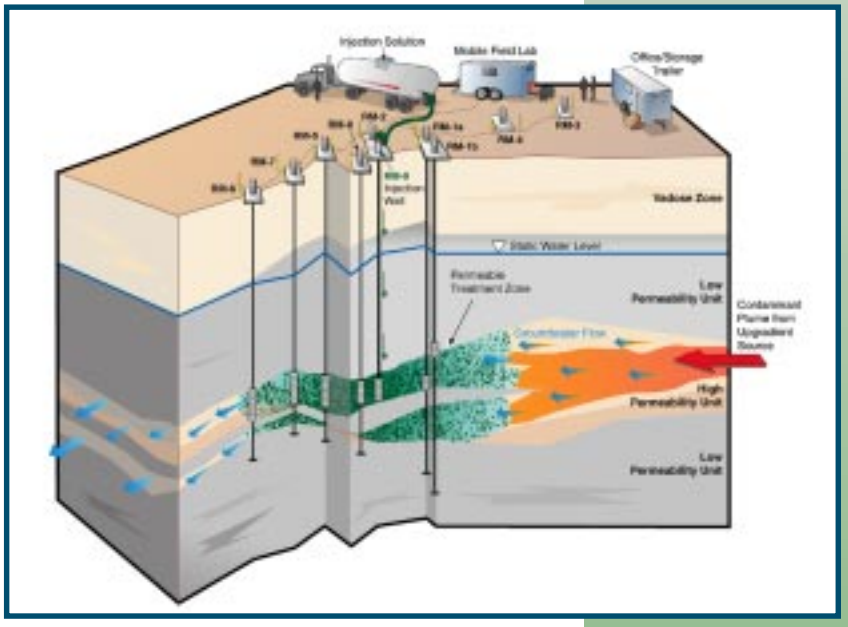
Treatment of Chromate Plumes at Hanford

ISRM has been successfully tested and deployed at the Hanford Site in southeastern Washington State to remediate a chromate plume threatening the Columbia River. The work proceeded in three phases: 1) a pilot-scale test was conducted at the 100-H Area, 2) a treatability test was performed at the 100-D Area, and 3) a full-scale deployment is underway at the 100-D Area.

With funding from DOE's Office of Science and Technology (Subsurface Contamination Focus Area), PNNL performed an initial pilot-scale test and

A related technology under development by PNNL injects micron-size iron into an aquifer using a specially designed viscous shear-thinning polymer. This technology may be applicable for sites with insufficient naturally occurring iron. It also may be possible to use the technology in conjunction with ISRM to speed the reaction of contaminants in the treatment zone.

subsequent treatability test. For the initial test, twenty-one thousand gallons of buffered sodium dithionite solution were injected into the unconfined aquifer at the 100-H Area. Core data indicated 60 to 100% of the available reactive iron in the treated aquifer sediments was reduced by the injected dithionite.



More than three years after injection, groundwater in the treatment zone remains anoxic. Hexavalent chromium levels in the groundwater remain below detection limits, with total chromium levels in the 1 to 3 ppb range.

The treatability test was conducted for treatment of chromium-contaminated groundwater in the 100-D Area. An ISRM test barrier was installed in 1998, with dimensions of 150 feet (length) by 50 feet (width) by 15 feet (thickness at a depth of 80-100 feet). The treatment zone was emplaced within the chromium groundwater plume, downgradient from the 1,000 ppb isopleth. The maximum concentration of chromium in the groundwater in May 1996 was 2020 ppb.

With ISRM, chromate concentrations measured within the treatment zone were less than the method detection limit (<8 ppb). Measurements from downgradient wells have shown and continue to show decreased chromate concentrations.

Full-scale deployment will create a 2,300-foot-long linear barrier at the 100-D Area by coalescing a number of smaller treatment zones. The project currently underway is funded by DOE's Office of Science and Technology and DOE Hanford. PNNL is supporting Bechtel Hanford, Inc. in the ISRM full-scale deployment.

Treatment of TCE Plume at Fort Lewis

The feasibility of using ISRM to treat groundwater contaminated with dissolved TCE has been tested at the U.S. Army's Fort Lewis Logistics Center. Extensive lab tests and an initial field test using dithionite treated sediments have shown potential, with a reduction of TCE concentrations in the field of up to 92% on the downgradient side of the reduced zone, from a background concentration of approximately 140 ppb to approximately 11

ppb. TCE destruction was confirmed by the presence of acetylene, the principal degradation product, and a high degree of iron reduction detected through analysis of sediment samples collected from post-test boreholes.

The Fort Lewis project indicated a number of key factors affect the overall design and efficiency of the ISRM technique. The Fort Lewis sediments contain a relatively high amount of available iron. TCE destruction is affected by the percentage of available iron that is treated (e.g., 40% appears to be the "break-through" value). Also, the Fort Lewis groundwater is relatively cold. Lower ambient aquifer temperature (11°C) retards iron reduction and degradation kinetics.

Long-term monitoring data collected following the field test indicate the emplaced treatment zone was partially reoxidized much sooner than predicted, based on bench-scale results and the quantity of reagent injected. Reasons for this premature reoxidation may include: 1) the Fort Lewis ISRM test site is located in a hydrogeologically complex setting (highly heterogeneous) and 2) high and seasonally variable groundwater velocities have been observed (as high as 8 feet/day).

The efficacy of the ISRM technology in treating other dissolved chlorinated solvents (PCE, cis-1,2-DCE, carbon tetrachloride, and TCA) has been successfully tested at the laboratory scale.