EMSP
Environmental Management Science Program
Project Summary Fact Sheet • October 1999

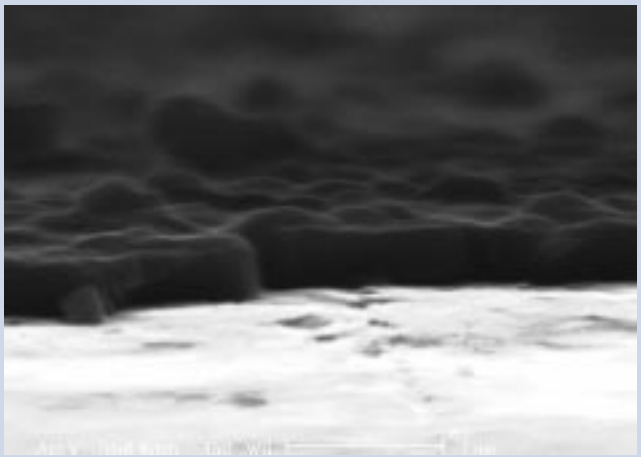
IN-SITU, PASSIVE FLOW, REACTIVE TREATMENT BARRIERS

Reactive barriers minimize operational costs for remediation and can be used where pumping is impractical

The subsurface barriers in this category are designed to perform reactions on mobile contaminants without using a physical barrier to prevent their flow. Although radionuclides and metal ions cannot be destroyed, reactive barriers can convert them to less mobile forms or cause them to bind to the barrier material. In addition, many organic compounds can be converted to safe products. These barriers are particularly appropriate where there is no infrastructure to support decades-long pump-and-treat methods.

Although reactive barriers are already being demonstrated at several U.S. Department of Energy (DOE) sites, including Rocky Flats and Oak Ridge, few fundamental studies of the applicable chemistry have been conducted. The projects described here are studying the fundamental aspects of current barrier technologies as well as obtaining basic information about factors that affect the mobility and reactivity of contaminant species:

- The detailed chemical mechanisms of the process of using potassium permanganate for in-situ oxidation of chlorinated solvents are being explored.
- The effects of several commonly used complexing agents on the mobility of uranium and other metal ions in the subsurface are being investigated.
- A detailed study of the mobility of strontium under various subsurface conditions has led to a suggestion that amorphous silica at higher pH values may provide a barrier to strontium migration.
- Finely divided iron has already been field tested at several sites, and the fundamental aspects of its use are being explored. One study has focused on the surface chemistry of several metal ions and chlorinated organic compounds on iron surfaces. Synergistic applications of bioremediation and iron surfaces for chromate reduction are also being explored.



Fundamental Surface Chemical Reactions
This scanning electron microscope image illustrates the use of iron for remediation of uranium dissolved in groundwater. The image, provided by the University of California project, shows a uranium oxide film, ~1 µm thick, grown atop an iron substrate by immersion under controlled conditions into a solution containing uranyl ions.

Problems/Solutions

- Needs for reactive barriers for strontium-90 have been cited at Brookhaven National Laboratory and at Hanford. A study of the factors that affect the subsurface migration of ^{90}Sr may lead to the development of improved barrier materials.
- Potassium permanganate is known to be an effective oxidizing agent for some chlorinated organic compounds, but competing reactions may limit its use as a barrier reactant. One project is investigating the detailed chemical mechanisms for dechlorination of chlorinated ethylenes and potential interferences from other naturally occurring organic substances.
- Reactive barriers have been demonstrated at commercial and DOE sites for the past decade, but not many fundamental studies of the applicable chemistry have been conducted. Several projects are directed toward gaining a basic understanding of the chemical processes in the reactive barriers currently being tested.

Anticipated Impact

- Zero-valent iron barriers are already being evaluated at DOE sites, as described in TMS #46, #2155, and #2156 [http://ost.em.doe.gov/tms/]. A detailed understanding of the chemistry that occurs on iron surfaces may lead to more efficient use of this material.
- Strontium-90 is one of the main radioactive contaminants of concern in the subsurface at Hanford, and in-situ treatment may be required if contamination extends to depths where excavation costs become prohibitive. One project is working to enhance the effectiveness of the barrier technologies already being studied.
- Reactive barriers are being evaluated at Rocky Flats, Oak Ridge Y-12/S-3 Ponds, the Kansas City Plant, and other DOE sites. Several projects may lead to improved understanding of methods to increase barrier effectiveness as well as development of new barrier technologies.

Systems for Remediating Chlorinated Solvents in the Subsurface

Potassium permanganate is a commonly used oxidizing agent, and previous workers have suggested its use for in-situ oxidation of chlorinated solvents. The goals of the Ohio State University/Duke Engineering Services project are to unravel the detailed chemical mechanism of the oxidations and to assess the potential of this reaction for deployment in the subsurface. The team has found pathways for rapid and complete dechlorination of various chlorinated ethylenes, and they have studied the competition with other naturally occurring organic substances for the oxidation reaction.

Systems for Immobilizing Radionuclides

Designing a reactive barrier for radioactive contaminants requires a detailed understanding of which forms of the contaminants are the most mobile. The Stanford University team has focused on the effects of certain widely used complexing agents on the mobility of uranium, and they find that the sorption behavior of uranyl is affected by chelators such as citric acid. They have also studied the effects of other complexing agents on the mobility of lead and strontium.

The objective of the work by the Lawrence Livermore National Laboratory/Arizona State University team is to determine the mobility of strontium-90 as a function of temperature and solution chemistry. Through characterization of the chemical species formed when strontium is adsorbed to a variety of components found in soils, sediments, and aquifers, the team has found that Sr has minimal retardation at mineral-water interfaces and that mobility is high when it is bound to colloids in slightly basic waters. The results also suggest that an amorphous silica reactive barrier at higher pH values may effectively trap Sr.

Reactive Barriers Containing Zero-Valent Iron

Several subsurface reactive barriers that use metallic iron filings are being developed for the removal of dissolved metals and chlorinated organic solvents from groundwater. The objective of the project at the University of California – Riverside is to determine the fundamental surface chemical reactions that are involved in order to optimize the remediation process. They investigated the removal of selenate, chromate, and uranyl ions employing state-of-the-art surface science techniques to study reacted iron. They determined the fundamental chemical mechanisms involved in contaminant removal, and have found that the elimination of dissolved atmospheric gases from solution is critical in extending the lifetime of the iron surfaces. In addition, the development of a novel method for the growth of uranium oxide films has been an important by-product of this research.

The University of Maine team has studied the possibility of combining iron filings or steel wool with sulfate-reducing bacteria (SRB) to produce a permeable, reactive barrier that could prevent migration of certain toxic metal ions. To gather the fundamental data required for this objective, they have studied the rates of reduction of chromate by iron(II) and metallic iron. They have found that the combination of SRB with steel wool exhibited better performance for chromate reduction than the same system without the SRB. The addition of lactate as a metabolite for the SRB also improved the performance.

Project Teams

Lead Principal Investigator (Award Number)

- Ohio State University
  PI: Frank W. Schwartz (54585)
  Duke Engineering Services
- Stanford University
  PI: James O. Leckie (54860)
- University of California – Riverside
  PI: Jory A. Yarmoff (55061)
- University of Maine
  PI: Lenly Weathers (55071)
- Lawrence Livermore National Laboratory
  PI: Susan Carroll (55249)
  Arizona State University

EMSP

Office of Science & Technology
Office of Environmental Management
U.S. Department of Energy

For additional information about the EMSP, please contact one of these representatives:

Mark A. Gilbertson
Director, Office of Science & Risk
(202) 586-7150
emsp@id.doe.gov
www.em.doe.gov/science

Tom Williams
EMSP Director, DOE-ID
(208) 526-2460
emsp@id.doe.gov
www.id.doe.gov/emsystems/emsp

Roland Hirsch
EMSP Director, Office of Science
(301) 903-9009
emsp@id.doe.gov
www.er.doe.gov