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IN SITU REDOX MANIPULATION: ENHANCEMENT OF CONTAMINANT DESTRUCTION AND IMMOBILIZATION

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NEED: The objective of this project is to develop, test, and evaluate in situ methods for immobilizing inorganic contaminants (metals, inorganic ions, and radionuclides) and destroying nitrates organic contaminants, (primarily chlorinated hydrocarbons). This research work is being performed for the U.S. Department of Energy through the In Situ Remediation Integrated Program is needed because:

- Groundwater treatment is the highest priority for the remediation of DOE sites.
- The baseline technology, pump and treat is expensive and ineffective.
- In situ remediation technologies are promising, but require development prior to demonstration and deployment.

CONCEPT: Chemical reagents and/or microbial nutrients will be injected into the subsurface to create a reducing environment in a portion of the Hanford unconfined aquifer. In this manner, a permeable treatment barrier will be created in situ, which could enhance destruction or immobilization of certain contaminants (see Figure 1). This type of in situ barrier has the advantage over other types of treatment methods of placing the contaminant- treatment capacity where it is most needed. Several important Hanford contaminants, including carbon tetrachloride, chloroform, trichloroethylene, chromate, technetium, and uranium are amenable to treatment in this manner. The ultimate goal of this project will be a small field test at the Hanford Site in conjunction with the VOC-Arid Integrated Demonstration at the 200 West Area carbon tetrachloride (CCl_4) site.

BACKGROUND: Subsurface contaminants at Hanford and other DOE sites occur in both the vadose and groundwater saturated zones. Common contaminants in the vadose zone include cesium, strontium, plutonium and chlorinated solvents. Common contaminants in groundwater plumes include chromate, uranium, technetium and nitrates. Chlorinated solvents are also found in the groundwater in some locations. Many of the groundwater plumes are already dispersed over large areas (square miles), and located hundreds of feet below the ground surface. This type of dispersed, inaccessible contamination, which is more difficult than other types of contamination to treat with excavation or pump-and-treat methods, is a prime candidate for in situ remediation. Therefore, the first focus for the field manipulation experiments is proposed to be the saturated zone of the Hanford unconfined aquifer. For example, if the aquifer can be made chemically reducing, chromate could be immobilized by

reduction to highly insoluble chromium hydroxide or iron chromium hydroxide solid solution (Sass and Rai, 1987). This case is a particularly favorable one, because chromium is not easily reoxidized under ambient environmental conditions. In addition, nitrate could be reduced to molecular nitrogen, and uranium and technetium could be reduced to less soluble and mobile forms. Finally, laboratory studies have shown that carbon tetrachloride and other chlorinated solvents can be degraded by microbes if the redox potential is reduced to the point where nitrate acts as an electron acceptor in place of oxygen (Bouwer and McCarty, 1983).

INITIAL PROPOSED FIELD TESTS: Two field tests are proposed for the initial stage of the project. The objective of the proposed tests is to manipulate the redox potential of the Hanford unconfined aquifer. Parameters to be determined include the nature of the reactions which occur, and the efficiency with which they are induced by the reagent or nutrient. The kinetics of the reduction and subsequent reequilibration of the aquifer will also be determined. The two experiments will be performed to compare two different approaches. One will involve reduction of the aquifer redox potential using abiotic chemical reagents. The other will involve accomplishing the reduction through stimulation of subsurface microflora. The two approaches are potentially applicable to different contaminant scenarios. The microbial reduction is probably more relevant to organic contaminants; whereas, the abiotic reduction is more applicable to inorganic contaminants, such as chromate and uranium. In addition, it is possible that the abiotic reagent will be unable to react efficiently with the aquifer solid phases at ambient pH's of the Hanford unconfined aquifer due to a lack of adsorption of the reagent. In this case, bacterially mediated reduction would be more effective.

CHEMICAL-REDUCTION TEST: The chemical-reduction test involves the use of a chemical reductant to reduce a small volume of the saturated zone. As shown recently for a sand-and-gravel aquifer by Barcelona and Holm (1991), nearly all the oxidizing or reducing capacity of an aquifer system resides in the solid mineral phases that comprise the aquifer matrix rather than in the groundwater. However, in spite of the small contribution of groundwater to the aquifer redox capacity, the most practical and non-invasive way of altering the aquifer redox status is to alter the chemistry of the groundwater that contacts the mineral solids. The reagent would first act to reduce oxidized species in the aqueous phase, and then would react to reduce ferric iron in minerals and oxide coatings in the aquifer. During the course of the experiment, aqueous phase species will be monitored to determine the progress of the reactions. Core samples will be taken at the end of the reaction phase of the experiment to determine the effects on the solid phases.

MICROBIAL-REDUCTION TEST: Investigation of microbial subsurface reduction processes for the field manipulation project will focus on the activities of dissimilatory bacteria (DIRB). This group of organisms was chosen for several reasons, including: their potential to transform or degrade mixed and complexed radioactive contaminants, their ability to function in anaerobic environments, and their ability to use an electron acceptor [Fe(III)], which is abundant in Hanford subsurface sediments. As microorganisms metabolize

organic or inorganic compounds in a closed or diffusion-limited environment, they use up all available oxygen, producing anaerobic conditions. Anaerobic microorganisms use alternative compounds, such as nitrate, sulfate and ferric iron, as electron-acceptors under these conditions. DIRB are a little-studied group that reduce ferric iron to ferrous forms as the terminal electron-accepting reaction in their metabolism (Nealson and Myers, 1992) . The resulting soluble ferrous iron can diffuse through an environment, carrying out reduction reactions, which may help to immobilize other metals. In addition, recent studies have shown that DIRB can directly reduce other metals, including uranium, to less soluble forms (Lovely et al. 1991).

For the microbial reduction test, a carbon source would be added to the aquifer to achieve a reduction of the redox potential. The heterotrophic bacteria would metabolize the carbon source, consuming dissolved oxygen and creating anoxic conditions in the process. Once the redox potential of the aqueous phase is reduced, mineral associated iron reducing bacteria could catalyze the transfer of electrons to the solid phases. The kinetics of the reactions and byproducts indicative of microbial catalysis would be monitored. Once again, core samples would be taken to determine the effects on the solid phases.

PROPOSED REAGENTS: For use in the proposed experiments, the reagents chosen must, of course, be effective in controlling the desired aquifer parameters. In addition, the reagents must either be chemically benign (e.g. oxygen or citrate) or must have good prospects for reacting to form benign products (e.g. sulfite or oxalate). For the abiotic experiment, the proposed reagent is sodium dithionite. Dithionite is highly reactive, so its persistence in the aquifer will be low. It reacts to form sulfate, which is non-toxic and already present in Hanford groundwater. For the biotic experiment, the proposed reagent/nutrient (carbon source) is either citrate or glucose, depending on the results of preliminary laboratory experiments. Both are non-toxic and are metabolized to carbon dioxide.

APPROACH: The basic approach involves injection-withdrawal, single-well, reactive tracer tests. The reagent is pumped into the aquifer, allowed to react for a period of time determined by the bench-scale tests, and then pumped back out. Measurements of the aqueous phase are made periodically in the monitoring wells during reaction and drift, and in the injection well during withdrawal. It is also important for this project to understand the reactions of the solid phases in the aquifer, so after reagent withdrawal, cores will be drilled to obtain solid samples. This approach allows for greater control over the travel of the reagent, and involvement of a minimum volume of the aquifer. It is also easier to interpret because the initial and boundary conditions are well defined. After reagent withdrawal, the rates of reequilibration will be monitored using indicator species in the aqueous phase. The reagent is pumped into the aquifer in a circle approximately twenty meters (sixty feet) in diameter. The injection well is screened over a five-foot interval. The monitoring wells are screened over a larger fifteen-foot interval in case there is any vertical diffusion of the plume. This scale and geometry would require injection of approximately 25,000 gallons of water containing the reagent, assuming twenty-five percent porosity for the formation. The water would be withdrawn from the injection well and the

aquifer allowed to equilibrate before the experiment. At the end of the reaction period, the reagent is pumped back out through the central injection-withdrawal well.

PRE-INJECTION ACTIVITIES: Prior to any drilling or injection, a variety of activities are either ongoing or planned. First are laboratory experiments using the proposed reagents and nutrients on Hanford sediments. These experiments will provide an understanding of the chemical and microbiological processes involved in the reactions as well as their rates and the efficiency with which they occur. The experiments will then be repeated in an intermediate-scale facility in order to determine the effects of scale and geometry. The proposed experiment will be modeled using several computer codes in order to optimize the experiment. Several parameters can be optimized, including maximum reagent withdrawal, minimum water withdrawal and optimum reagent concentration. Finally, a series of field characterization activities will be performed, including use of data from nearby existing and proposed wells, characterization of cores from drilling of the injection/withdrawal well, hydrologic characterization tests and conservative tracer tests.

EXPECTED RESULTS: Expected results include determination of the feasibility of using natural geochemical and microbial processes to reduce solids in the Hanford unconfined aquifer. Data will be obtained on the processes and kinetics of the reduction reactions and on the subsequent reequilibration of the system. Quantitative information on redox reactions and the redox capacity of Hanford subsurface sediments will be derived. And finally, a comparison of the abiotic and biotic methods for controlling redox potential in the subsurface will be made.

SUMMARY: In summary, a field experimental site to study the manipulation of natural subsurface processes will be designed and constructed at the 200-West Area at Hanford. The emphasis of the initial proposed experiments is to test the feasibility of controlling the redox potential of the Hanford unconfined aquifer using chemical reagents and microbial nutrients. The ability to achieve this control will have implication for in situ remediation of dispersed aqueous contaminants at Hanford. No long-term effects on the aquifer or to groundwater quality are expected.

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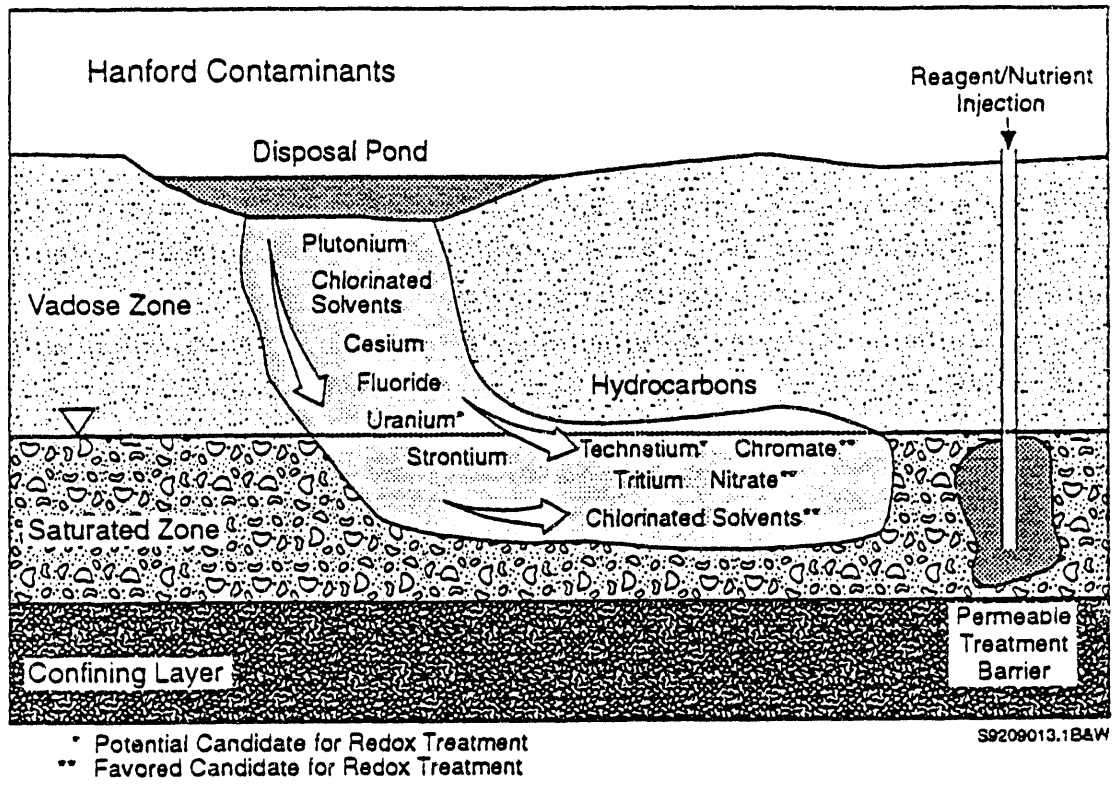

FIGURE 1 Conceptual Diagram of an In Situ Permeable Treatment Barrier

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