WATER RESOURCES RESEARCH GRANT PROPOSAL

(1)   Title: TreaTment of Nitrate-Contaminated Groundwater Using ZERO-VALENT IRON and Autotrophic Denitrification

(2)   Focus Categories: GW, NC, TRT, WQL.
(3)   Keywords: Biological Treatment, Groundwater, Indigenous Microorganisms, In Situ Remediation, Nitrate, Nitrite, Reactive Barriers.
(4)   Duration: September 1, 1998 to August 31, 2000 (24 months)
(5)   FY 1998 Federal Funds: $ 60,000 $60,000 $ 0
            (Requested Funds)   Total   Direct   Indirect
(6)   FY 1998 Non-Federal Funds: $120,086 $82,682 $37,404
            (Allocated Matching Funds)   Total   Direct   Indirect
(7)   Principal Investigator:

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(8)   Congressional District: 1st
(9)   State/Regional Water Problems to be Addressed.

Nitrate is a priority pollutant due to its potential to cause methemoglobinemia. There is also circumstantial evidence linking nitrate ingestion to gastric cancer and birth defects (Mirvish, 1985). Nitrate contamination is a major water quality problem in the United States, especially in the North Central Region (Nolan et al., 1997). In Iowa alone, 1 million tons of nitrogen are applied each year, and 18% of the private wells contain nitrate above the drinking water standard of 10 mg/l as N. Another 37% of the wells have levels greater than 3 mg/l as N, typically considered indicative of anthropogenic pollution (Kross et al., 1993). The ubiquity of the nitrate contamination problem is reflected in a 1985 AWWA survey, which found that 23% of all primary drinking water standard violations in the United States were due to high nitrate concentrations (Kapoor and Viraraghavan, 1997). Without appropriate cleanup measures, nitrate can persist in subsoils and endanger groundwater resources and public health. Therefore, there is considerable public interest and regulatory pressure to clean up nitrate-contaminated aquifers. Several physical-chemical and biological processes have been proposed for this purpose (e.g., reverse osmosis and ion exchange). However, traditional treatment processes are relatively expensive to operate and are limited by the production of nitrate-concentrated waste streams that may pose a disposal problem. This provides a strong motivation to explore novel nitrate-removal alternatives that addresses both physical-chemical and microbiological advantages and constraints.

Encouraging results in laboratory and field experiments have stimulated a very rapid increase in the use of Fe(0) as a reactive material to remove redox-sensitive contaminants from groundwater. Semipermeable Fe(0) barriers are particularly attractive for *in situ* remediation in that they conserve energy and water, and through long-term low operating and maintenance costs, have the potential to be considerably less costly than conventional

cleanup methods. Fe(0) can be placed in the path of a contaminant plume, either on a trench (O'Hannesin and Gillham, 1992), buried as a broad continuous curtain (Blowes et al., 1995), or injected as colloids (Kaplan et al., 1994), to name a few options. This approach has been used to remove waste chlorinated solvents (e.g., Gillham and O'Hannesin, 1994; Johnson et al., 1996) and hexavalent chromium (Powell et al., 1995). We recently reported that a similar approach can also be used to treat nitrate-contaminated water (Till et al., 1998). Specifically, we showed that Fe(0) can stoichiometrically reduce nitrate to ammonium, and that cathodic hydrogen (produced during anaerobic Fe(0) corrosion by water) can sustain microbial denitrification to reduce nitrate to more innocuous products (i.e., N_2O and N_2). Consequently, combining Fe(0) with hydrogenotrophic denitrifying bacteria might significantly enhance the nitrate removal process by increasing removal rates and improving the end product distribution. Nevertheless, our limited knowledge of microbial ecology in Fe(0) systems preclude us from taking full advantage of such beneficial biogeochemical interactions. To this end, we need to answer numerous questions. Some questions are related to the feasibility of bioaugmenting Fe(0) barriers with specialized strains (e.g., Do we need to add hydrogenotrophic denitrifiers or will an indigenous hydrogenotrophic consortium eventually develop around Fe(0) barriers to fill a metabolic niche associated with nitrate-based respiration? How long does it take for such a natural hydrogenotrophic consortium to develop?). Other questions should be addressed to obtain basic criteria for process design and operation (e.g., How thick should the barriers be? How long does Fe(0) or the added bacteria remain active? How does pH, temperature, and redox conditions affect nitrate removal kinetics and end product distribution? How do other contaminants or naturally occurring substrates affect the removal efficiency? How does bacterial growth affect the hydraulic performance?). Finally, there are basic mechanistic questions that should be answered to contribute to the rational development of reactive barriers as a waste management technology (e.g., How do bacteria affect the reactivity of the Fe(0) surface? How does Fe(0) corrosion affect microbial population dynamics? Can we predict with reasonable certainty that what we want to happen, will happen?). This project will initiate a research program to investigate the answers to these numerous questions.

(10)   Benefits/Information Derived.

This project will develop a new and efficient method to remediate nitrate-contaminated aquifers. This approach is based on combining a novel chemical process (reductive treatment with Fe(0)) with a promising biological process (autotrophic, hydrogen-fueled denitrification). While the development of a cost-effective and sustainable approach to remove nitrates from contaminated water resources has great intrinsic merit, this project has also significant extrinsic merit associated with the insight it will provide for enhancing the general performance of reactive barriers. For example, preliminary results and theory suggest that combining Fe(0) with hydrogenotrophic anaerobic bacteria also has a great potential to remove many other redox-sensitive contaminants, such as chlorinated solvents (Weathers et al., 1997), Cr(VI), sulfate, nitroaromatic explosives (TNT and RDX), technetium, and uranium. Specifically, the production of cathodic hydrogen during anaerobic corrosion of Fe(0) represents an increase in the bioavailability of an excellent primary substrate to support microbial reduction of the target contaminants and the further degradation of intermediate products that may accumulate

following reaction with Fe(0). Hydrogenotrophs could also remove the passivating cathodic H_2 layer from the Fe(0) surface (i.e., cathodic depolarization), which could enhance the reactivity of Fe(0). Therefore, while this project will focus on the dynamic interactions between Fe(0), nitrate, and hydrogenotrophic denitrifiers, it will also serve as a model system to advance our understanding of biogeochemical interactions in reactive Fe(0) barriers. An important corollary benefit will also be the insight gained on the dynamics of anaerobic microbial communities in response to normal environmental variation and novel anthropogenic changes.

Batch experiments will delineate the applicability and limitations of this technology, and provide a rational basis for the design and construction of biologically active Fe(0) barriers. The validation of the batch results using flow-through column experiments seeks to confirm the feasibility of the process. Finally, this project will train one graduate student and will serve as the basis for his/her dissertations. Hence, directly and indirectly, this project will contribute to improvements in the "Nation's scientific and engineering research, education and human resource base".