USGS WATER RESOURCES RESEARCH GRANT PROPOSAL

A. Research Proposal

Title: In-situ Destruction of Solvents by Permanganate Oxidation

2. Focus Categories: GW, TS, HYDGEO

3. Keywords: ground water, DNAPL, in-situ remediation, oxidation, potassium permanganate

4. Duration: 9/98-9/00

5. Funds Requested: (Federal \$28,409 yr 1, \$26,658 yr 2)

6. Non-federal Funds Pledged: (\$115,726)

7. Principal and Co-Principal Investigators:

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8. Congressional District: Ohio 15th

9. Statement of Critical Regional Water Problem:

The contamination problems posed by chlorinated solvents are well known. When dissolved in contaminant plumes, chlorinated solvents pose an extremely difficult challenge for hydrogeologists attempting to remove them from the subsurface. First, even low aqueous concentrations could be greatly in excess of the public drinking-water standards, although many chlorinated solvents are sparingly soluble in water. Thus, a large volume of ground water can be contaminated by a small volume of spilled solvent. Secondly, due to their stability and persistence in the subsurface, pools and residual solvents can remain over many decades, or even centuries and serve as a long-term source of continued groundwater contamination. Finally, chlorinated solvents typically do not move along the flow gradient in aquifers because they are denser than water and tend to move downward under a separate hydraulic head.

Industries and government agencies alike have an important stake in research related to the clean up of chlorinated solvents at contaminated sites. Many severely contaminated sites remain to be cleaned up in the United States and around the world. The main motivation for research on alternative technologies is that some conventional schemes (like pump-and-treat or in situ bioremdiation) have limitations in dealing with solvent contamination. For example, the undetected presence of DNAPL at a site generally relegates pump-and-treat schemes to an effort in hydraulic plume control rather than mass recovery. Bioremediation schemes have been difficult to implement. Potential problems or limitations of such approaches involve metabolite toxicity, competitive cosubstrate inhibition, and difficulties in process optimization for aerobic conditions.

Thus, formidable challenges remain in developing schemes for the clean up of DNAPL sites. Other conventional approaches like soil vapor extraction and gas sparging work well when site conditions are appropriate. In summary, there remains a need for research to develop approaches to treat contamination due to both free phase and dissolved solvents.

10: Statement of Results or Benefits:

The proposed study will contribute to knowledge by:

(*i*) providing an assessment of the efficacy of permanganate flooding for DNAPL destruction, and the factors contributing to success or failure,

(ii) elucidating the problems and opportunities associated with variabledensity flow in injection withdrawal schemes, and

(iii) improving our ability to visualize contaminant distributions and patterns of flooding using novel monitoring schemes.

This paragraph discusses these points in more detail. History in the development of remedial technologies has shown time and time again that there is a rush to move promising technologies into the field before fundamental scientific work has been completed. We believe that this practice has wasted resources and botched site cleanups. Given the potential of permanganate oxidation of organic compounds as a remediation scheme, we believe that fundamental studies of the type proposed here are warranted. The proposed study addresses to an important extent the perceived weaknesses of the permanganate schemes – flooding inefficiencies and pore plugging, related to reaction products. A unique feature of the proposed study is its experimentally-based orientation. It is difficult to dispute the historical importance of experimentation in the study of hydrogeological processes. Yet, in relation to problems of coupled flow and reactive transport, there has been a preference and probably an overemphasis on the use of mathematical models to explore processes. Besides new insight gained through the experiments themselves, I expect that the actual data will be important both for model validation and theoretical analyses. A variety of potential remedial technologies involve the injection of fluids (e.g., surfactant and alcohol flooding, co-solvent addition in bioremediation). Yet, through much of this work there is at best a vague understanding or at worst no understanding of how even small fluid-density differences can lead to complex flow and mixing, as well as inefficient displacement processes. This problem is even more complicated in heterogeneous media. An important strand of the proposed

study is concerned with the arrangement and operation of injection/withdrawal wells to optimize flooding efficiencies. Moreover, we will examine the impact of heterogeneity on patterns of variable density flow. This knowledge will help provide practical schemes for improving the efficiency of a variety of remediation schemes. The final area where the proposed study will contribute is in the development or improvement of technologies for monitoring both solid and liquid phase concentrations in flow-tanks and ultimately in the field. Previous NSF-supported studies of coupled phenomena led to the development of some interesting new optical and electrical approaches. Clearly, progress in development of remedial technologies both in the laboratory and the field will require an ability to monitor the space/time variation of key chemical parameters. Both the image and electrically-based monitoring schemes have potential to contribute such highly resolved data. The present study will extend our knowledge in this respect as we apply these techniques for the first time to multi-phase systems and deal with practical problems of robustness of probes in solvents.