Project: ID# 54699 The Use of Dielectric and NMR Measurements To Determine the Pore-Scale Location of Organic Contaminants

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Graduate Students: Over the past 3+ years this project has involved two graduate students, 1 research associate, 1 post-doctoral fellow.

Research Objective

A critical step in achieving the cost-effective treatment of a contaminated region of the subsurface is obtaining accurate information about the location and extent of subsurface contaminants. In many cases non-invasive means of subsurface characterization are required. This research addresses fundamental scientific issues that are central to the use and interpretation of dielectric and nuclear magnetic resonance (NMR) measurements as a means of detecting organic contaminants. We focus on the potential use of these methods to detect small amounts of adsorbed organic contaminants. The specific objective of our three-year research project was to investigate, through laboratory and theoretical studies, the effect of adsorbed organics on the dielectric and nuclear magnetic resonance (NMR) response of porous geological materials.

Research Progress and Implications

This report summarizes the work completed over the past 3.5 years of our project. Summarized below are the results of a series of studies designed to address our research objective.

Measurement of the Dielectric Constant

Laboratory measurements were made, in the frequency range 500 Hz to 10 MHz, of the dielectric constant of samples of sand and kaolinite clay; these sample were prepared with varying amounts of adsorbed oil and saturated with a 0.001 M NaCl brine. Previous research had suggested that the optimal way to determine the effect of adsorbed organics on dielectric measurements is to isolate the dielectric response of the "wetted" solid phase from the measured dielectric response of the total solid/fluid mixture; the "wetted" solid includes the response of the solid/fluid interface. Using an inclusion-based effective medium theory we were able to extract the dielectric response of the wetted solid from the experimental data. We found that the presence of sorbed oil had little effect on the dielectric response of the wetted sand matrix, presumably because of the very low surface area (0.2 m^2/g) of the solid/fluid interface. In contrast, the kaolinite (with a surface area of 5-12 m^2/g) data indicated a consistent decrease in the dielectric constant of the wetted solid phase as the amount of oil sorbed onto the solid surface was increased.

The results from this experimental study show that the presence of sorbed oil leads to a detectable change in the dielectric properties of saturated, high surface area geologic materials, and could lead to new ways of using dielectric measurements in the detection of contaminants.

Measurement of NMR Relaxation Times

Proton nuclear magnetic resonance (NMR) is a non-invasive technique that can be used in the laboratory or in the field to characterize porous geological materials. The NMR parameter

of specific interest in our study is the measured relaxation time T of the water in the porous geological materials, which is described by the following equation: $1/T = 1/Tb + \rho\ S/V$, where Tb is the relaxation time of the bulk water, S/V is the surface area to volume ratio of the pore space, and ρ, the surface relaxivity, is a measure of the ability of the surface of the pore space to enhance the relaxation rate of the water (1/T). Our working hypothesis throughout this study was that the presence of adsorbed organics would change the surface relaxivity (ρ).

An important first step in our research was to determine the influence of paramagnetic species, typically present in the near-surface environment, on NMR measurements. This issue was addressed through an extensive set of laboratory experiments in which we measured the NMR response of sands containing controlled amounts of paramagnetic Fe(III), present as adsorbed Fe^{3+} ions, solid Fe(III) oxyhydroxide surface coatings and separate Fe(III)-containing mineral grains. We found that each type of paramagnetic impurity had its own constant surface relaxivity and that the fraction of the sand surface populated with paramagnetic sites controlled the surface relaxivity of the sand. These results provide information about the effect of Fe(III) on NMR data that must be taken into account in order to accurately interpret NMR measurements in the near-surface environment. We anticipate that these results will be widely used as NMR is increasingly applied to address near-surface environmental problems.

To test our hypothesis that the adsorption of organic contaminants will affect the surface relaxivity of a geological material, we measured the NMR response of a water-saturated sand in its "clean" state and with various amount of adsorbed oil. For natural sand samples, with small concentrations of iron surface impurities, the surface relaxivity dropped sharply with increasing thickness of the adsorbed oil layer. We found that NMR could detect less than one complete monolayer of adsorbed crude oil (as little as 20 microgram/m^2) on silica gel if the silica surface was coated with a paramagnetic substance such as iron(III) oxyhydroxide; suggesting that NMR measurements could be a useful way of detecting trace amount of adsorbed organic contaminants.

Planned Activities: This project is in its final year; we received a one-year extension for the period September 1999 to September 2000. The next few months will be spent conducting a final set of experiments, completing our theoretical modeling, and submitting two papers for publication.

Information Access:

Traci R. Bryar, Christopher J. Daughney and Rosemary J. Knight, Paramagnetic effects of iron(III) species on nuclear magnetic relaxation of fluids in porous media. Journal of Magnetic Resonance, **142**, 74-85 (2000). http://www.idealibrary.com/links/doi/10.1006/jmre.1999.1917

Christopher J. Daughney, Traci R. Bryar and Rosemary J. Knight, Detecting sorbed hydrocarbons in a porous medium using proton nuclear magnetic resonance. Environmental Science and Technology, **34**, 332-337 (2000). http://pubs.acs.org/reprint-request?es990637m/o72D