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The Use of Dielectric and NMR Measurements to Determine the Pore-Scale Location of Organic Contaminants

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Research Objective

The objective of our three-year research project is to investigate the effect of adsorbed organics on the dielectric and nuclear magnetic resonance (NMR) response of porous geological materials. This will allow us to assess the use of dielectric and NMR measurements at a site to determine whether organic contaminants are present in the central volume of the pore space or are adsorbed to the solid surfaces. In addition, we propose to use laboratory dielectric and NMR measurements to study the kinetics of the adsorption and desorption of organics.

Research Progress and Implications

This report summarizes work completed after 20 months of a three-year project. Our research involves the study of the NMR and dielectric behavior of sands with three types of solid surfaces: water-wet, where water spontaneously coats and adsorbs to the solid surfaces; hydrophobic, where water is repelled from the solid surfaces by an organosilane coating; and oil-wet, where oil coats the solid surfaces. The oil-wet case is representative of a contaminated soil, in which oil has become adsorbed to the solid surfaces.

We have completed the development of reliable and re-produceable procedures for sample preparation for the NMR and dielectric measurements. Water-wet sand samples are prepared using either a natural quartz sand, reagent grade pure quartz sand or silica gel. These solids are sequentially rinsed in 10% HCl, 10% NaOH, and distilled water, then oven-dried, in order to remove impurities and homogenize their surfaces. Hydrophobic samples are prepared by reacting water-wet solids with 5% octadecyltrichlorosilane in toluene for 48 hours at 110°C. Oil-wet samples are prepared by exposing the hydrophobic samples to a suspension of crude oil in toluene-heptane-alcohol. In addition to the preparation of samples with a homogeneous surface, we have developed a procedure that allows us to control and monitor the amount of oil adsorbed to a water-wet surface. In this procedure, a known weight of water-wet solid is simultaneously exposed to an aqueous phase (0.01 M NaCl) and an organic phase (toluene-heptane) containing a known concentration of oil.

The key experimental variable in our experiments is the state of the solid/fluid interface. The size of the interface is equivalent to the surface area of the solid, which for the natural sand and pure quartz sand is approximately 1 m2/g, and for the silica gel is approximately 200 m2/g. As a means of characterizing the solid/fluid interface, we perform acid-base titrations to determine the magnitude of the electric charge at the solid surface, and its relation to the pH of the surrounding solution. The water-wet solids display roughly 2 x 10^{-6} equivalents of charge per m^2 surface area and are all positively charged below pH 2 and negatively charged above pH 2. The hydrophobic surfaces display acid-base behavior which indicates that there is essentially no electric charge at the hydrophobic surface, regardless of solution pH. The oil-wet solids display a charge of 5 x 10-7 equivalents/m^2, roughly half the charge of the water-wet solids, and are positively charged below pH 5 and negatively charged above pH 5.

One of the central issues in our research is to understand how and why NMR measurements are affected by the wettability of the solid surface. The measured NMR parameter for a porous, fluid-saturated sand sample is the T1 proton relaxation time, which can be related to the material properties of the sample by the equation:

$$\frac{1}{T_1} = \rho \frac{S}{V} + \frac{1}{T_{1b}}, \qquad (1)$$

(1) where r is the surface relaxivity, S/V is the surface area to volume ratio of the pore space and T1b is the relaxation time for the bulk pore fluid. The NMR parameter that is expected to be closely related to the state of the solid surface is r, which can be considered to be a measure of the ability of the surface to shorten the relaxation time. Previous work has suggested that r should be highest in water-wet systems and should decrease in oil-wet or hydrophobic systems. These studies however neglected to account for the role of the chemistry of the solid and fluid.

In our experiments with water-wet pure quartz sand and water-wet silica gel, we have found that r is close to zero (approximately 10^{-4} mm/s) and is constant over all pH values. For the pure quartz sand, with its very low surface area to volume ratio (S/V), we found that the measured relaxation time T1 (2.9 s) is the same as the bulk fluid relaxation time T1b within experimental error. For silica gel, with a much larger S/V, T1 decreased to 1.6 s. This set of experiments has conclusively shown that the larger values of r commonly reported for natural sands cannot be explained by the presence of water-wet solid surfaces alone.

The factor that must be accounted for in order to interpret and use NMR measurements on natural sands is the effect of paramagnetic species, which can be present in the pore fluid, as separate mineral grains, as ions adsorbed to sand surface sites or as a thin layer of solid precipitated onto the sand grains. The relaxation time of bulk fluids containing Fe^{3+} was found to decrease exponentially with increasing concentration. This illustrates the importance of accounting for the chemistry of the pore fluid in interpreting NMR measurements of fluid-saturated materials. When insoluble iron(III) titanium oxide grains were mixed with silica gel at pH 5.7, T1 decreased exponentially from 1.6 to 0.6 s with increasing fraction of paramagnetic mineral (0 to15% by weight). This decrease in T1 was caused by a dramatic increase in r due to the presence of paramagnetic solid surfaces, with no change in the wettability of the surface. In order to study the effect of adsorbed paramagnetics, pure quartz sand was equilibrated with 0.5 ppm Fe^{3+} solution at pH 1 and at pH 3. At pH 1 no iron was adsorbed to the surface and T1 remained the same as T1b; but at pH 3, 5-20% of the iron was adsorbed and T1 decreased 0.7 s due to an increase in r. We can conclude that a paramagnetic ion adsorbed to the sand surface has a much greater effect on relaxation than a dissolved paramagnetic ion. This experiment also shows that the surface charge of the solid surface affects NMR indirectly by affecting the adsorption of paramagnetic ions.

Having documented the effect of paramagnetics, we can develop a better understanding of the effect of oil-wet surfaces on NMR measurements. Here again we find that paramagnetic species play an important role in relaxation processes, both through changes in the pore fluid chemistry and through the addition of paramagnetic species to the solid surface. A series of experiments with oil-wet materials is in progress at this time.

Dielectric measurements are, in general, less sensitive than NMR to molecular-scale interactions at the solid/fluid interface. As a result, our approach has been to first complete the NMR component of our study, in order to develop a clear understanding of the physics and chemistry of the various solid/fluid systems. In the first set of dielectric experiments, conducted with water-wet, hydrophobic and oil-wet quartz sands, we found that the change in the electrical conductivity of the pore fluid, due to chemical equilibration with the three types of surfaces, was the dominant factor in the dielectric measurements. As a result, the dielectric constant of the oil-wet sand was much greater than that of the water-wet sand. In repeat experiments, the pore fluid chemistry has been set to eliminate this effect. We find that the presence of an oil-wet or hydrophobic surface causes a decrease in the dielectric constant at frequencies greater than 100 kHz, but an increase at lower frequencies. We are presently investigating the role of surface conduction associated with the properties of the oil-water interface in oil-wet sands.

Planned Activities

In months 20 to 26 of this project we plan to complete the NMR experiments with the oil-wet and hydrophobic sands. In months 22 to 26 we will conduct NMR experiments as a function of temperature, to assess the use of NMR as means of monitoring the adsorption and desorption of organics. In month 26 we will select NMR experiments that will be repeated using a lower field spectrometer, and these will be conducted in months 26 to 30. The dielectric experiments, which will parallel the

NMR experiments, will continue through month 32. The last four months of the project will be spent on analysis, interpretation, and modeling of data and preparation of final papers/reports, with some time spent as needed to repeat specific measurements.