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

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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 measures 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 specifically focus on the potential use of these methods to detect small amounts of adsorbed organic contaminants.

The 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 response of porous geological materials.

Dielectric Response of Sand and Clay with Sorbed Oil

Sample Description

- natural sand from Wedron Silica Sand Company 99.88% silicon dioxide, surface area 0.2 m^2/g
- kaolinite from Source Clay Mineral Repository $Al_4[Si_4O_{10}](OH)_8$, surface area 5 - 12 m^2/g

- samples prepared with varying amounts of adsorbed crude oil
- cylindrical parallel-plate sample holder
- gold-sputtered copper electrodes, d = 4.225 cm; Plexiglass ring, h = 0.448 cm
- vacuum-saturated with a 0.001 M NaCl brine

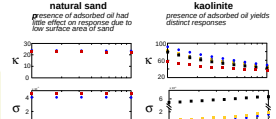
Measurements

- Hewlett Packard 4192a low frequency impedance analyzer
- laboratory measurements in frequency range 500 Hz to 10 MHz

Data

κ = measured dielectric constant

σ = measured conductivity [S/m]



Modeling

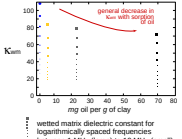
goal to determine the effect of adsorbed organic contaminants on dielectric measurements

approach isolate the dielectric response of the "wetted" solid matrix (κ_{wm} and σ_{wm}) from the measured dielectric response of the total solid/fluid systems

method inclusion-based effective medium theory

Results

- kaolinite data indicate a general decrease in the dielectric constant of the wetted solid phase κ_{wm} as the amount of oil on the solid surface increases



wetted matrix dielectric constant for logarithmically spaced frequencies between 1 MHz (large) to 10 MHz (small)

Summary

- presence of adsorbed oil leads to a detectable change in the dielectric properties of saturated, high surface area geologic materials such as kaolinite
- results are encouraging for the potential use of radar field techniques to quantify the presence of sorbed contaminants in the subsurface

Previous Work / Hypotheses

Dielectric Measurements

- dielectric constant κ of saturated geologic materials depends on volume fractions and dielectric constants of individual components
- wetting of the solid with ~ 1nm of water contributes to κ
- define κ of the wetted solid matrix κ_{wm}
- κ_{wm} has been found to be proportional to the water-wetted surface area

To Test adsorption of oil will reduce κ_{wm} (through reduction of water-wetted surface area)

if yes

Can measurement of κ_{wm} be used to quantify the presence of sorbed oil?

NMR Measurements

- measured parameter is T, relaxation of water in porous geological materials:

$$1/T = 1/T_b + \rho\ (S/V)$$

T_b = relaxation time for bulk water
ρ = surface relaxivity, or ability of surface to relax water molecules
S/V = surface area-to-volume ratio of the pore space

- ρ is due to paramagnetic sites on solid surface
- ρ has been found to change with wettability of rocks

To Test adsorption of oil will cause decrease in ρ

if yes

Can measurement of ρ be used to quantify the presence of sorbed oil?

Significant Results & Conclusions

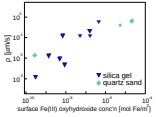
- ★ **The dielectric constant of clay was found to be very sensitive to small amounts (<10 mg/g) of adsorbed oil. Dielectric measurements using radar methods may be useful as a non-invasive means of detecting trace amounts of sorbed, residual contaminant.**
- ★ **NMR measurements on silica gel found that the adsorption of oil (as little as 15 $\mu g/m^2$ of surface) caused a measurable decrease in ρ. NMR measurements have great potential as a means of direct detection of organic contaminants. Significant improvements are needed in our ability to collect and interpret NMR field data.**

Effect of Sorbed Oil on NMR Relaxivity ρ

Effect of paramagnetic species on ρ

Samples
- silica gel • pure quartz sand
- prepared with varying amounts of surface Fe(III) oxyhydroxide (paramagnetic)

Observations
- with no surface Fe(III), ρ ~ 0.01 μm/s (very low)
- ρ increases with surface concentration of Fe(III)
- for comparison, ρ of natural rocks = 1 - 20 μm/s

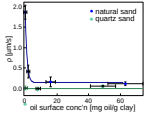


Effect of oil coating on ρ

Samples
- pure quartz sand • natural sand (Wedron Silica Sand Company)
- prepared with varying amounts of adsorbed oil

Observations
- quartz sand - no paramagnetic sites on solid surfaces
  - very little change in ρ (0.07 μm/s)
- natural sand - naturally occurring paramagnetic sites on solid surface (~ 0.002 mol Fe / m^2)
  - ρ very sensitive to sorbed oil, decreases by 1.1 μm/s

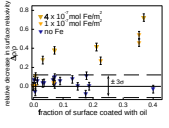
Conclusions
- ρ decreases with sorbed oil if and only if paramagnetic sites are on surface
- sorption of oil "shields" water from paramagnetic sites



Effect of small amounts of adsorbed oil on ρ

Samples
- silica gel with no Fe
- silica gel with 1 x 10^{-3} mol Fe / m^2
- silica gel with 4 x 10^{-3} mol Fe / m^2
- all prepared with varying amounts of adsorbed oil

Observations
- silica gel with no Fe
  - sorption of oil causes no change in ρ; $\Delta\rho = 0 \pm 3\sigma$
- silica gel with Fe
  - ρ decreases with sorption of oil
  - adsorbed oil concentration as low as 15 $\mu g/m^2$ decreases surface relaxivity by 25% compared to the same solid without oil



Additional Information

Information Access

Traci R. Bryar, Christopher J. Daughney and Rosemary J. Knight, Paramagnetic effects of iron(III) on nuclear magnetic relaxation of fluids in porous media. Journal of Magnetic Resonance, **142**, 74-85 (2000). http://www.idealibrary.com/links/toc/jmre/1999/1917

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