Laboratory studies of the effect of sorbed oil on proton nuclear magnetic resonance

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ABSTRACT

Proton NMR (nuclear magnetic resonance) measurements were made of T_1 and T_2 relaxation times of water in saturated sands containing varying amounts of sorbed oil on the grain surfaces. The porosity, surface area, and grain density of the sands and the relaxation times of the extracted pore water were also determined experimentally. Sorption of oil changed the relaxation time of water in the saturated sands through changes in surface area and surface relaxivity, the parameter used to quantify the ability of the surface of the pore space to reduce NMR relaxation times. In some cases the addition of oil to the surfaces decreased the surface area, an observation that suggested the oil was coating the surface in a way to reduce surface roughness. When larger amounts of oil were added to the surface, surface area increased. The changes in surface relaxivity with the amount of sorbed oil were governed by the relaxivity of the clean, oil-free surfaces. In the Wedron sand, with a surface relaxivity typical of naturally occurring sands, the relaxivity decreased with the addition of oil to the surface of the sand grains. In the A–A sand, a clean, pure quartz sand, the relaxivity increased from a very low value for the oil-free sample to a higher value, interpreted to be that of the oil surface.

INTRODUCTION

One of the challenges currently facing the scientific and engineering communities is the development of effective strategies for dealing with organic contaminants in the subsurface of the earth. To treat or remediate a contaminated site, information is required about the pore-scale location of the contaminant, i.e., is the contaminant present as a bulk fluid occupying the central volume of the pore space or is the contaminant sorbed to, or coating, the solid surface. The location of the contaminant has a large effect on its mobility and needs to be considered in the se-

lection and design of a remediation technique. Given the risks associated with drilling and direct sampling, there is considerable interest in the use of noninvasive geophysical methods as a means of obtaining the required information about subsurface contaminants.

Of specific interest in our research is the use of proton NMR (nuclear magnetic resonance) to detect sorbed organic contaminants. NMR measurements have been made using borehole logging instruments in the petroleum industry since the 1960s (Brown and Gamson, 1960), with significant improvements in the technology in the 1990s. A surface loop instrument is being investigated for near-surface and environmental applications (Schirov et al., 1991). As is done in this study, laboratory NMR measurements are commonly used as a way to study and interpret NMR field measurements.

The measured NMR parameters in which we are interested are the relaxation times of the water molecules, referred to as T_1 and T_2. For water in a single pore in a rock or soil, the relaxation rate $1/T_1$ is the rate at which the net magnetization of the proton magnetic moments returns to its equilibrium state. Time T_1 is determined by a combination of processes acting in the bulk water and at the pore surface (Senturia and Robinson, 1970; Brownstein and Tarr, 1979):

$$\frac{1}{T_1} = \frac{1}{T_{1b}} + \rho_1 \left(\frac{S}{V} \right), \tag{1}$$

where T_{1b} is the relaxation time of the bulk pore water, S/V is the surface area-to-volume ratio of the pore, and ρ, the surface relaxivity, can be interpreted as the ability of the pore surface to enhance relaxation. When NMR relaxation measurements are made on water in a porous geologic material with a range of pore sizes, there will be a distribution of relaxation times. Multiexponential relaxation of NMR signal intensity I with time t is observed (Timur, 1969):

$$I(t) = \sum_i A_i \exp(-t/T_{1i}), \tag{2}$$

where each A_i is proportional to the amount of water with relaxation time T_{1i}. For practical reasons, T_1 measurements are

difficult to make with borehole or surface loop instruments, so field applications of NMR typically involve measurements of T_2. The value $1/T_2$ is the rate at which the proton magnetic moments dephase. The expression for T_2 requires an additional term to account for the internal field gradients (G) experienced by diffusing fluid molecules:

$$\frac{1}{T_2} = \frac{1}{T_{2b}} + \rho_2\left(\frac{S}{V}\right) + \frac{D_{eff}}{3}(\gamma_H G t_E)^2, \qquad (3)$$

where D_{eff} is the effective diffusion coefficient (for restricted diffusion), γ_H is the gyromagnetic ratio of the hydrogen nucleus, and t_E is the echo spacing of radio-frequency pulses used for data collection (Kenyon, 1997). For this study G was approximately zero, making the third term in equation (3) negligible.

There have been previous studies of the change in NMR relaxation times of water in porous materials resulting from changes in the state of the solid–fluid interface. A number of studies showed an increase in NMR relaxation times as mineral surfaces were changed from water wet to hydrophobic or oil coated (e.g., Brown and Fatt, 1956; Borgia et al., 1991; Hsu, 1994; Howard, 1998; Kanters et al., 1998; Zhang et al., 2000; Guan et al., 2002). One study by Hsu (1994) found a decrease in relaxation time when a glass bead pack was coated with bitumen (Texaco Inc.). We build on this previous work to develop an understanding of the way in which the sorption of varying amounts of an organic contaminant is likely to influence measured NMR relaxation times. Our working hypothesis is that there are two dominant ways in which the sorption of a contaminant can change the NMR response of a material; we conduct a series of laboratory experiments to test this hypothesis.

One way in which the sorption of a contaminant could affect the relaxation time is through a change in the size of the solid–fluid interface. As shown in equation (1), the NMR relaxation time of water in a geologic material is closely related to the geometry of the pore space, through a dependence on S/V. The change in surface area with the addition of an organic contaminant and its effect on NMR has not previously been reported.

The second way in which we suggest that the sorption of a contaminant could change the NMR relaxation time is by causing a change in ρ. The primary control on ρ in geological materials is known to be the concentration of paramagnetic species such as Fe(III) and Mn(II), with Fe(III) being the most common paramagnetic species contained in minerals in the near-surface region of the earth. It has been shown that ρ increases with surface concentration of paramagnetic sites (e.g., Foley et al., 1996). Based on theoretical studies (Neue, 1988; Korb et al., 1997) we expect ρ to decrease as the distance between the water molecules and the paramagnetic sites increases. The sorption of a contaminant could therefore increase the NMR relaxation time by physically separating the water molecules from the surface paramagnetic sites. This explanation was proposed as an explanation for the decrease in T_1 observed by most researchers (e.g., Brown and Fatt, 1956).

If the contaminant contains a higher concentration of paramagnetic impurities than the original solid surface, the sorption of a contaminant could increase ρ and correspondingly decrease relaxation time. The increase in T_1 relaxation time seen in the study by Hsu (1994) was attributed to an increase

in ρ_1 because of the high paramagnetic content of the adsorbed asphaltenes. We suggest therefore that three factors determine the change in ρ: the concentration of paramagnetic sites on the solid surface, the thickness of the surface coating of the contaminant, and the paramagnetic content of the contaminant.

This experimental study investigates two possible ways in which the sorption of an organic contaminant can affect measured NMR relaxation times, via a change in S and/or ρ. Equation (1) indicates that changes to S and ρ have equal potential to affect relaxation time. We determine the change in both S and ρ as various amounts of oil are added to the surfaces of sand grains and use our experimental results to assess the use of NMR measurements as a means of monitoring the sorption of organic contaminants.

EXPERIMENTAL METHODS

Sample description and preparation

Two sands were used in this study. The first is a naturally occurring sand, referred to as the Wedron sand, obtained from Wedron Silica Co. in Illinois. The specifications for this sand describe it as 99.88% silicon dioxide with 0.1% clay and silt and 0.010% CaO. Whole-rock analysis by X-ray fluorescence (ASL Chemex, North Vancouver, Canada) indicated 0.22% Fe_2O_3 (1.5 mg Fe/g). The Wedron sand was sieved to obtain a narrow distribution of grain sizes, 106–125 μm in diameter.

The second sand was a pure quartz sand, produced by Alpha-Aesar to be 99.995% silicon dioxide and referred to as the A-A sand. We treated the A-A sand further to make sure it contained as few paramagnetic impurities as possible; it was repeatedly rinsed in 10% hydrochloric acid, distilled and deionized water, and was then oven dried. The A-A sand had a grain size of 75 to 300 μm and was not sieved so as to avoid any contamination.

The crude oil that was used as the contaminant was Cold Lake bitumen, supplied by Imperial Oil (Calgary). The bitumen was minimally processed to remove inorganic particles and water. It is a highly viscous, petroporphyrin-rich crude with 15% asphaltene content (Semple et al., 1990; Khulbe et al., 1996). The bulk oil contains paramagnetic impurities as iron (120 μg/g) and vanadium (190 μg/g) ions (determined by ASL Ltd., Vancouver). However, it is primarily the asphaltene fraction of the oil that adsorbs to the sand surfaces. The paramagnetic content of asphaltenes consists of approximately equal quantities ($\sim 10^{18}$ spins/g) of VO^{2+} and organic free radicals (Khulbe et al., 1996). The density of the asphaltene fraction is 1.0 g/cm^3 (Rhodes, 1992).

Four different methods were used to prepare samples with varying amounts of oil sorbed to or coating the surfaces of the sand grains; the details of the procedures are given in the Appendix. In this work, each oil-coated sand is referred to by the name of the method used to prepare it, that is, the Daughney, Bryar, hydrophobic, and Kanters methods. The Daughney method results in oil being sorbed to the mineral surfaces in trace amounts that are less than or equal to one monolayer of oil; the thickness of a monolayer for the oil used in this study is on the order of 1 nm. The Bryar method is designed to produce a coating of oil on the surfaces at least one monolayer thick. The hydrophobic method begins by first making the sand surfaces hydrophobic; this method results in oil coatings which are thicker than those obtained using the

Bryar method. The Kanters method results in very thick oil coatings.

The density of the solid grains (δ_g) of each of the untreated and treated sands was calculated using measurements on a porous sample of known total volume; the error in each case was determined from replicate measurements. The mass of the grains was measured and the volume occupied by the grains determined using a helium pycnometer (Micromeritics, model 1305). In the case of samples with an oil coating, the solid grains included the oil. The amount of oil present in each of the prepared sands, expressed as mass of oil per gram of untreated sand (m_{oil}/m_u), was calculated with the following equation:

$$\frac{m_{oil}}{m_u} = \frac{\delta_{oil}}{\delta_{g,u}}\left(\frac{\delta_{g,u}V_{oc} - m_{oc}}{m_{oc} - \delta_{oil}V_{oc}}\right), \tag{4}$$

where V_{oc} is the volume occupied by the grains of oil-coated sand (including the oil), m_{oc} is the mass of those grains, and δ_{oil} and $\delta_{g,u}$ are the densities of the oil coating and the untreated sand grains, respectively. In the case of the sample prepared using the Daughney method, the amount of oil sorbed to the surface was too small to cause a detectable change in volume of the solid grains; the sorbed oil reported was the amount of oil lost from the solution used to prepare the sand, as determined by spectrophotometry (see the Appendix).

The specific surface area (S_s), which is the surface area per unit mass of the material, of the sands was determined using krypton gas adsorption (Micromeritics ORR 2100D surface area analyzer) and calculated from the adsorption isotherm using the Brunauer-Emmett-Teller (BET) equation (Brunauer et al., 1938). Repeat measurements on a standard with a specific surface area of $0.39\,\text{m}^2/\text{g}$ indicated an error of 10% ($\pm 0.04\,\text{m}^2/\text{g}$) for S_s.

NMR measurements and data analysis

Samples were prepared for NMR measurement by packing the sands into cylindrical Teflon sample cells of known volume. The porosity of each of the samples was determined from mass measurements of the packed sample cells before saturation. Each sand sample was saturated with 0.01 M NaCl brine and sealed to prevent water loss. After the NMR measurements on the saturated sands, the samples were centrifuged to remove the pore water. The NMR measurements were repeated on the bulk pore water.

The T_1 relaxation data were obtained with a 90-MHz, ^{1}H-NMR spectrometer (Bruker) using a modified inversion-recovery pulse program as described in Bryar et al. (2000). Data for each sample were collected at 23.7°C with 90 delay times ($t = 0.5$ ms to 12 s). The wait time between scans was 15 s to ensure complete relaxation. Both intensity and standard deviation of the intensity were recorded for each delay time; the S/N of the data was between 100 and 250.

To relate our laboratory results directly to measurements made using borehole NMR logging and surface loop NMR, T_2 at low field was measured for two of our samples at 25.0°C using a 1-MHz proton NMR spectrometer (Corespec 1000, NUMAR); these measurements were done by the Tomographic Imaging and Porous Media Laboratory (Calgary). The standard Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence was used with echo times (t_E) of 0.2, 0.3, 0.5, and 0.8 ms and a recovery time of 15 s; 5000 linearly spaced data points were collected for each experiment. The S/N of the data for saturated samples was between 70 and 100.

For each NMR measurement the raw decay curve [equation (2)] was fit to a distribution of 160 exponentially spaced T_1 values (ranging from 1 ms to 10 s) using Tikhonov regularized inversion as implemented by Whittall and MacKay (1989). Inversion parameters were selected so that each datum was misfit by approximately one standard deviation.

EFFECT OF OIL SORPTION AND COATINGS ON SURFACE AREA

Experimental results

The amount of oil on the grains in each sample is listed in Table 1. The sample prepared with the Daughney method contains a very small amount of oil. If we assume that the oil forms a uniform layer coating the grain surfaces, the thickness would only be 0.6 nm. The samples with the most oil, prepared with the Kanters method, represent an extreme case where all of the oil typical for contaminated sites (i.e., 50–64 mg/g: Wattiau et al., 1999; Dorn and Salanitro, 2000) is present as a coating on the solid grains rather than as a bulk fluid in the central volume of the pore space.

Table 1. Physical property measurements and calculated parameters.

Sample	Amount of oil (mg/g)	Specific surface area (m^2/g)	Density (g/cm³)	Porosity of NMR sample	Surface area-to-volume ratio of NMR sample (μm^{-1})
Wedron sand					
Untreated	0	0.095 ± 0.01	2.67 ± 0.02	0.417 ± 0.004	0.36 ± 0.04
Oil coated, Daughney method	0.06 ± 0.02	0.095*	2.67*	0.407 ± 0.004	0.37 ± 0.04
Oil coated, Bryar method	2.3 ± 0.4	0.0207 ± 0.002	2.64 ± 0.02	0.425 ± 0.004	0.07 ± 0.01
Oil coated, hydrophobic method	17 ± 3	0.0208 ± 0.002	2.59 ± 0.02	0.414 ± 0.004	0.08 ± 0.01
Oil coated, Kanters method	70 ± 10	0.638 ± 0.06	2.41 ± 0.02	0.474 ± 0.005	1.7 ± 0.1
A-A sand					
Untreated	0	0.188 ± 0.02	2.63 ± 0.02	0.453 ± 0.005	0.60 ± 0.06
Oil coated, hydrophobic method	9 ± 1	0.10 ± 0.01	2.59 ± 0.02	0.458 ± 0.004	0.31 ± 0.03
Oil coated, Kanters method	53 ± 9	0.39 ± 0.04	2.43 ± 0.02	0.515 ± 0.005	0.89 ± 0.09

*These values were not measured. The quantity of oil present was too small to make a measurable difference (from untreated Wedron sand) in the density or surface area.

The measured specific surface area values given in Table 1 illustrate the way in which the addition of oil to the solid grains changed the surface areas of the sands. The specific surface areas of 0.095 m²/g for the untreated Wedron sand and 0.188 m²/g for the untreated A–A sand are within the expected range for quartz sands. For both sands, the addition of oil to the surface with the hydrophobic method reduces surface area from that of the untreated sand, whereas the oil added using the Kanters method results in large increases in the measured surface areas. The amount of oil added with the Daughney method was insufficient to result in a detectable change in surface area (Daughney et al., 2000).

Discussion of the observed changes in surface area

Let us first consider the measured specific surface areas for the untreated sands and calculate, as a starting point in each case, the specific surface area for a sand of equivalent grain diameter d composed of smooth spherical grains; S_s is equivalent to $6/d\delta_g$. Using $d = 190\,\mu$m for the A-A sand, we obtain a specific surface area of 0.0195 m²/g, which is close to an order of magnitude less than the measured value of 0.188 m²/g. Using $d = 115\,\mu$m for the Wedron sand, we obtain a specific surface area of 0.012 m²/g, which is also significantly less than the measured value of 0.095 m²/g. The higher measured surface areas for both sands could be the result of the presence of high surface area materials such as clays, irregular grain shapes, and/or the surface roughness of the grains. There is no clay in the A-A sand, so the irregular shape and roughness of the grains must be responsible for the observed surface area. In the Wedron sand, the clay fraction (0.1%) would add to the surface area, but this fraction is low enough that the main contribution to surface area must again be grain shape and surface roughness.

The hydrophobic method reduced the surface area of the A–A sand by 47%, while both the Bryar and hydrophobic methods caused a 78% reduction in the surface area of the Wedron sand. We were unable to determine directly the geometry of the oil coating, but we interpret the observed changes as evidence that the oil coated the grains in such a way as to cover and smooth the surface, filling in some of the roughness and irregularities on the solid surfaces. When much more oil was added using the Kanters method (4–5 times more oil), the surface areas of both sands increased to values greater than those measured for the untreated surfaces. While again we have no direct measurement of the geometry of the oil coating, the Kanters method tends to produce a thick coating of oil that is then partially removed in such a way as to cause an increase in surface topography and a resulting increase in specific surface area. It is important to note that we are unsure whether this type of oil coating would form in natural environments.

EFFECT OF OIL SORPTION AND COATINGS ON NMR SURFACE RELAXIVITY

NMR results

Figure 1 shows the distribution of T_1 obtained for the water in saturated, untreated Wedron sand. The very simple, monomodal distribution is as expected for an unconsolidated sand sample with little or no microporosity. The T_1 and T_2 distributions for all other water-saturated samples in this study are similar, the position of the peak in the distribution being the only significant difference. We choose to represent the distribution by the logarithmic mean relaxation time which, for a distribution of the form shown in Figure 1, indicates the center of the peak in the distribution. The NMR relaxation times for the water in all of the samples are listed in Table 2. There was no separate peak for the oil in any of the samples because the amount of oil present was too small. The distribution obtained
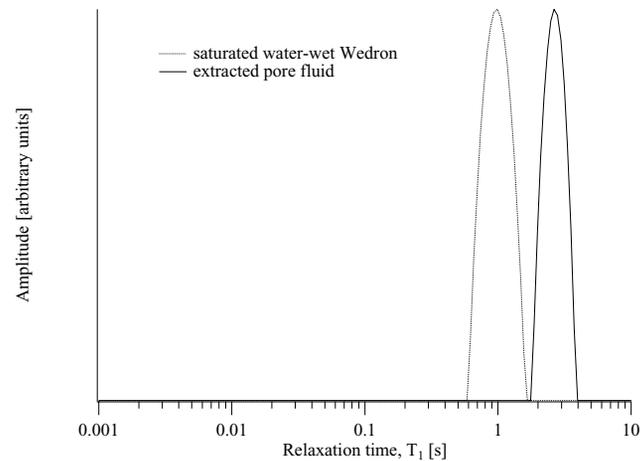

FIG. 1. NMR T_1 relaxation time distributions for bulk pore fluid and 0.01 M brine in fully saturated Wedron sand. Although amplitude of the peaks is proportional to the amount of fluid present, these distributions have been normalized to an arbitrary amplitude to facilitate comparison.

Table 2. NMR measurements and calculated surface relaxivity values.

Sample	90 MHz		1 MHz		Surface relaxivity	
	T_1 (s)	T_{1b} (s)	T_2 (s)	T_{2b} (s)	ρ_1 (μm/s)	ρ_2 (μm/s)
Wedron sand						
Untreated	0.988	2.845	0.257	2.55	1.9 ± 0.2	9.9 ± 0.9
Oil coated, Daughney method	0.967	2.60			1.8 ± 0.2	
Oil coated, Bryar method	2.44	2.64			0.4 ± 0.2	
Oil coated, hydrophobic method	2.71	2.81	2.50	2.55	0.2 ± 0.1	0.1 ± 0.1
Oil coated, Kanters method	1.74	2.786			0.13 ± 0.01	
A-A sand						
Untreated	$2.81 \pm 0.05^*$	2.88			0.01 ± 0.01	
Oil coated, hydrophobic method	2.72	2.83			0.05 ± 0.03	
Oil coated, Kanters method	2.40	2.80			0.07 ± 0.01	

*Average relaxation time and standard deviation based on six replicate samples.

for the pore water extracted from the untreated Wedron sand is also shown in Figure 1; this is typical of what was obtained for the pore water extracted from all of the samples. The log mean T_{1b} and T_{2b} values are listed in Table 2. Most relaxation times listed in Table 2 were obtained from an NMR measurement on a single sample. To obtain an estimate of error, we ran six replicate samples for the untreated A-A sand and defined the error for all relaxation time measurements as equal to the standard deviation in this set of measurements, which was 2%. The T_1 reported for water in this sand in Table 2 is the average of the six replicates.

The porosity value ϕ measured for each of the NMR samples is reported in Table 1 along with S/V, which was determined from experimentally measured values using

$$\left(\frac{S}{V}\right)_{pore} = \frac{1-\phi}{\phi} S_s \delta_g. \qquad (5)$$

Surface relaxivity ρ_1 values for all of the samples of Wedron and A–A sands were calculated from the S/V values and the T_1 and T_{1b} measurements using equation (1); ρ_2 was calculated using equation (3) with the known values of S/V, T_2, and T_{2b}. The T_2 distribution was constant for all echo times (t_E) from 0.2 to 0.8 ms, indicating that G $\sim$ 0 and the third term of equation (3) was negligible. All surface relaxivity values are listed in Table 2.

Discussion of the observed changes in surface relaxivity

For the untreated Wedron sand ρ_1 is 1.9 ± 0.2 μm/s; this value is within the expected range for sandstones (0.9–7.1 μm/s; Borgia et al., 1996). In contrast, ρ_1 for the untreated A-A sand is the extremely low value of 0.01 ± 0.01 μm/s. These two results are consistent with the fact that ρ_1 of a solid is largely determined by the concentration of paramagnetic sites on the surface of the grains. The Wedron sand, given its iron content, will contain paramagnetic impurities as do most naturally occurring sands. The A-A sand is composed of pure quartz and contains no paramagnetics. This value of $\sim$0.01 μm/s has recently been established as the lower limit for ρ_1 of a sand with no paramagnetic impurities (Bryar et al., 2000).

There are distinct differences in the way in which the values of ρ_1 of the two sands are affected by the presence of sorbed oil. Figure 2 illustrates the changes in these values with the
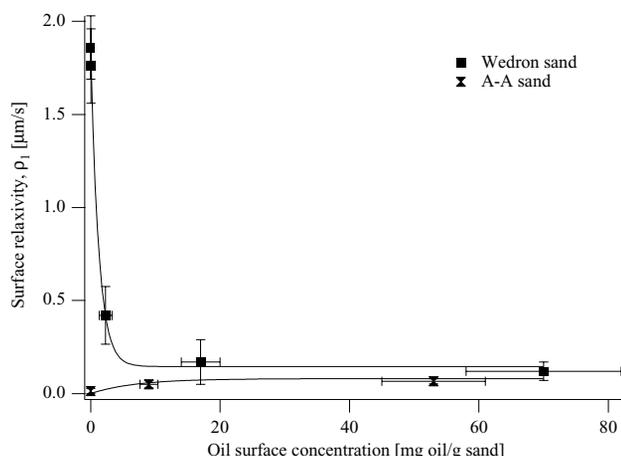
addition of oil to the solid surface. For the Wedron sand, ρ_1 consistently decreases from 1.9 to 1.8 to 0.4 to 0.2 to 0.13 μm/s as the amount of oil on the sand is increased by the use of the various sample preparation methods. In contrast, ρ_1 for the A-A sand increases slightly, from 0.01 to 0.05 to 0.07 μm/s, when prepared with the hydrophobic and Kanters methods. We suggest that this difference in response to an increase in the amount of oil on grain surfaces is because of the paramagnetic content of the two sands. In a material such as the Wedron sand, which contains paramagnetic impurities on the grain surfaces, existing theoretical models suggest that ρ_1 will decrease as the distance increases between the hydrogen atoms in the pore water and the paramagnetic impurities on the mineral surface. We suggest this is the effect we are observing in these data for the Wedron sand; the addition of oil to the surface physically separates the water molecules from the paramagnetic sites.

In the A-A sand with no paramagnetics, this model does not apply. A decrease in ρ_1 is not predicted to occur, nor is it seen in the data. To explain the observed increase in ρ_1, we suggest that, in the limit of a thick oil coating, the surface relaxivities of both sands approach the relaxivity of the oil surface itself. In our experiments, the relaxivity of the oil will be controlled by the presence of the organic radicals and paramagnetic vanadium species in the asphaltene component. Based on our data, we estimate ρ_1 of the oil surface to be $\sim$0.10 μm/s.

The trends in relaxivity discussed above were based on T_1 measurements made at 90 MHz, but NMR logging tools and the surface loop instrument typically measure T_2 at 0.5–2 MHz and $\sim$2 kHz, respectively. The results from low-frequency NMR measurements are given in Table 2 for the Wedron sand with (a) no oil and (b) 17 mg/g oil. The ρ_2 surface relaxivity of the untreated sand is 9.9 ± 0.9 μm/s, much higher than ρ_1 (1.9 ± 0.9 μm/s), but ρ_2 and ρ_1 for the oil-coated Wedron sand are almost the same ($\rho_1 = 0.2 \pm 0.1$ μm/s; $\rho_2 = 0.1 \pm 0.1$ μm/s). These observations indicate that the same amount of oil on the sand surfaces causes a change in relaxivity observed with T_2 measurements that is approximately five times greater than that observed with T_1 measurements. These results suggest that the low-frequency NMR logging tools and surface loop instrument might be more sensitive to changes in the amount of sorbed organic contaminants than high-frequency laboratory NMR.

CONCLUSIONS

Our laboratory measurements have shown the effects that oil sorption and coatings can have on both the surface area and relaxivity of a sand. We conclude that the addition of oil to the surface of a rock or soil can result in a change in measured NMR relaxation times through a change in one or both of these variables.

Our measurements of the surface areas of the sands used in this study indicate that it would be very difficult to predict the type of change in specific surface area that would be caused by the sorption of a contaminant. We suggest that the change in surface area will depend on the initial surface roughness of the material and on the specific way in which the contaminant is added to the surface. For example, surface area could decrease if the contaminant sorbs in such a way as to form a continuous surface coating that smoothes the surface topography, but it could increase if the contaminant forms irregular or uneven patches.

FIG. 2. NMR surface relaxivity versus concentration of sorbed oil for two different sands.

We found that changes in surface relaxivity with the amount of sorbed oil were primarily governed by the relaxivity of the clean, oil-free surfaces. In the A-A sand, a clean, pure quartz sand, the relaxivity increased from a very low value for the oil-free sample to a higher value, interpreted to be that of the oil surface. In the Wedron sand, with a surface relaxivity typical of naturally occurring sands, the relaxivity decreased with the addition of oil to the surface of the sand grains. These results suggest that for sands in natural environments the surface relaxivity should decrease with the sorption of an organic contaminant. The magnitude of the change in ρ with amount of contaminant cannot be predicted because it will depend on the paramagnetic content of the sand surfaces and the contaminant. Once large amounts of a contaminant are present, our data suggest that the surface relaxivity value will reach that of the contaminant and will become insensitive to the addition of more contaminant.

One of the objectives of our study was to assess the potential use of NMR measurements as a means of monitoring the sorption of organic contaminants. While we are confident that contaminant sorption will decrease ρ, our experimental results indicate that the change in surface area is less predictable. To interpret an increase in T_1 or T_2 as an increase in the amount of sorbed oil, it would be necessary to obtain the change in S from an independent measurement. The outstanding issue is our lack of understanding of the geometry of contaminants on mineral surfaces. Additional experiments are required to determine the spatial distribution of different contaminants as they sorb to geologic materials and their effect on surface area. With this new information, one might be able to relate changes in NMR relaxation times to changes in sorbed contaminants, provided that all other parameters which affect relaxation times (e.g., the porosity and the paramagnetic content of the sand) remain constant during monitoring.

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APPENDIX

PREPARATION OF OIL-COATED SANDS

Four different methods were used to prepare samples with oil coating the surfaces of the sand grains. The water used in this study was distilled and deionized with a measured resistivity of 18 MΩ-cm. All other chemicals were reagent grade (obtained from Sigma-Aldrich).

The first method, referred to as the Bryar method, involved drying the sand at 110°C, then mixing it, while still hot, with a 15% solution of crude oil dissolved in 1:1 (v:v) toluene : n-heptane. After the mixture cooled to room temperature, ethanol was slowly added until the solubility of the oil was reduced to the point where a suspension of oil barely formed. This precipitated the asphaltenes onto the sand surfaces. The mixture was vacuum filtered using a Buchner funnel and rinsed thoroughly with ethanol. The oil-coated sand was then dried in an 80°C oven overnight.

The second method, referred to as the hydrophobic method, started by treating the Wedron sand and A-A sand to make the naturally water-wet (hydrophilic) surfaces hydrophobic by silanizing the sands with trichlorooctadecylsilane (an 18 carbon silane). A mixture composed of 300 g of sand, 50 ml of silane, and 1.0 liter of toluene was refluxed at 110°C for 48 hours. The sand was then filtered, rinsed with toluene, and dried at room temperature. A byproduct of the reaction is hydrochloric acid, so the sand was then thoroughly washed with deionized water for several days and then dried in an 80°C oven. The hydrophobic sand was then treated in the same way as in the Bryar method.

The Kanters method is adapted from Kanters et al. (1998). Dried sand was mixed with an excess of crude oil, placed in a vacuum oven (500 mm Hg), and heated to 60°C for one day and then 80°C for 10 days. The nonasphaltene fraction of the bitumen was then rinsed from the oil with n-heptane, and the oil-coated sand was dried in an 80°C oven overnight.

The Daughney method is described in Daughney et al. (2000). In a 40-mL Teflon reaction vessel, 2.0 g of sand and 10.0 ml of 0.01 M NaCl were tumbled for three days at 25°C. The pH at this stage was 8 because of the buffering effect of the $CaCO_3$ in the Wedron sand. At this time, 25.0 ml of a 1:1 (v:v) toluene : n-heptane mixture with 278 μg oil/ml was added to each reaction vessel. The reaction vessels were tumbled for an additional three days before the organic phase was analyzed for oil by spectrophotometry at 402 nm, allowing the concentration of sorbed oil to be determined by difference: 0.06 ± 0.02 mg/g oil on Wedron sands. At the completion of this preparation, the reaction vessel stood with two immiscible fluid layers and the sand at the bottom. For the NMR measurement, wet sand was transferred from the reaction vessel to a glass NMR tube. The tube was centrifuged to pack the sample, and excess water was put aside for the bulk T_{1b} measurement.