DETERMINING CLAY TYPE BY USING LOW-FIELD NUCLEAR MAGNETIC RESONANCE

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ABSTRACT

The presence of movable fines may have an impact on oil production. This paper will show that low-field nuclear magnetic resonance (NMR) can be used to obtain information regarding the interactions between clays and the fluids they are exposed to. A comprehensive experimental program was conducted to determine differences in the interactions between different types of clays and different types of fluids (distilled and tap water and mild brine). The results show that the different isolated clay samples provide signature amplitude peaks in a transverse relaxation (T_2) distribution, despite similarity in particle size distributions. These results indicate that low-field NMR can be used to qualitatively identify the presence of clays in a sample and can indicate clay type. This information could prove to be useful in determining the methods in which to handle and analyse core samples.

INTRODUCTION

The term “clay bound water” commonly denotes the water that moves freely between weakly bonded molecular layers in a clay and causes clays to swell and shrink with the addition and removal of water [1]. Recent experiments have shown it is possible to fully represent clay bound water in transverse relaxation (T_2) distributions from an NMR relaxometer [2]. This bound volume can significantly affect the calculation of producible and non-producible fluid volumes because when calculating these two parameters it is assumed that no producible fluid remains in the pores once displaced from a rock under a certain pressure [3]. While many believe this phenomenon is partly due to clay type, some researchers suggest that clay morphology instead is responsible [4].

MATERIALS AND INSTRUMENTATION

Illite and kaolinite clays were obtained from Ceramics Canada in Calgary, AB and supplied by Plainsman Clays in Medicine Hat, AB. The illite-rich clay (IRC) is mined from Ravenscrag, SK while the kaolinite-rich clay (KRC) is mined in Troy, Idaho [5]. The montmorillonite-rich clay (MRC) is a sodium-based source clay originating from Arizona that was obtained from the University of Missouri [6]. Clay compositions are shown in Table 1 with the balance from the chemical analysis being organics lost on ignition.

NMR measurements were made with the Corespec 1000™ at a frequency of 1 MHz (field strength is 0.024 T). Duplicate runs were performed during each measurement in order to ensure results were genuine and not a result of experimental artifacts. The data was processed using EchoFit v. 3.02, a software package created by NUMAR Corporation, a subsidiary of Halliburton, which employed the non-negative least squares method to create the T_2 distributions.

Particle size distributions were performed in duplicate with the Malvern Instruments Mastersizer 2000 Particle Analyser, a laser diffraction analyser capable of detecting particles in the range of 0.02 μm to 2000 μm.

PROCEDURE

A representative sub sample was used to determine particle size distributions. Each sample was poured into a glass vial 3.5 cm in diameter and 5.0 cm in height and the sample was packed slightly so that the column was slightly less than the length of the homogeneous region of the magnet in the CoreSpec 1000^{TM}. An NMR measurement was taken to determine the signal amplitude the sample alone produces. Distilled water, tap water and brine consisting of 5% NaCl were also measured separately in the CoreSpec 1000^{TM}. Fluid was added at a rate of approximately 1 drop per second until the sample reached 10wt% saturation. So the samples are only partially saturated, not 100% or vacuum saturated. The lid of the vial was placed and wrapped several times with Teflon tape in order to minimise water loss as a result of evaporation. The vials were placed in a sealed beaker in an effort to further minimise evaporation. NMR measurements were taken every half hour for four hours, then every hour for four more hours. The next day fluid was added drop wise until the sample reached 15wt% saturation and NMR measurements are taken at the same times as the day before. On the third day fluid was added drop wise until the sample was at 20wt% saturation. Higher saturation values were not used since the focus of this work was on clay bound water. In other words, this work emphasises analysis of the bound fluid [7]. NMR measurements were taken using the same schedule as the two previous days. The CPMG pulse sequence was used to eliminate effects due to local variations in the magnetic field. The NMR parameters used in this program are shown in Table 2. These are not typical parameters to use when analysing samples that contain water. Time-echo of 0.3 ms is the lowest value that will still provide reliable data. Post-train delay has been shortened because the objective in this program was to obtain information at lower T_2 values, which corresponds to signals given off from fluids in small pores or bound to grain surfaces.

RESULTS

Figure 1 shows the particle size distributions the three clays. This figure shows that IRC has a large fraction of the particles are approximately 7 μm in size, although a significant portion of the particles are approximately 50 μm in size. The particle size distributions of KRC and MRC have one peak at 10 and 15 μm, respectively. The median particle diameter for IRC, KRC and MRC are 13.92, 10.36 and 13.04 μm, respectively.

The spectra obtained before adding fluid show very low signal amplitudes, likely due to background noise or resident water. If this was due to water alone the signal from the dry state constitutes 0.7% of total dry sample weight at the most, which is not significant. This indicates that oven drying the clays before beginning the NMR experiments was not necessary.

The NMR spectra of the clays immediately after adding tap water are shown in Figure 2. This figure, also representative of occurrences immediately after adding distilled water and mild brine to the clays, shows that the amplitude peak always appears at a higher T_2 value after adding 10wt% fluid compared to after 15 and 20wt% of fluid is introduced. This is most likely due to the fact that the sample is dry prior to adding 10wt% fluid, whereas the clays are already wet when an additional 5wt% of fluid is added.

Figure 3 shows the NMR spectra of the clays at various tap water saturations after reaching equilibrium. This figure shows that the spectra obtained after the addition of fluid were uni-modal, as expected [2]. This is because there was not enough water added to reside in the larger pores as a bulk phase. All of the samples showed amplitude peaks at T_2 values below 10 ms, which indicates the presence of microporosity and agrees with the findings of other researchers [8]. It is apparent that the amplitude peaks for all three samples do not move significantly over time or with changes in saturation. This was typical regardless of the fluid added to the clays. In other words, NMR response is not affected by the changes in salinity presented in this experimental program. Another feature that appeared without consideration for the salinity of the fluid is that the montmorillonite produced amplitude peaks at the lowest T_2 values (approximately 1 ms), followed by kaolinite then illite (5 and 6 ms, respectively). Other researchers have determined that montmorillonite produces amplitude peaks at T_2 values in the sub-millisecond range, illite displays peak T_2 values of 1 – 2 ms and kaolinite showed amplitude peaks at T_2 values greater than 3 ms at a frequency of 1 MHz [4, 9]. The spectra for swelling clays like montmorillonite are an indication of the water in the inner hydration shells of exchangeable cations in the interlamellar space [1, 2]. Figure 3 shows that the peaks for kaolinite and illite appeared at 5 and 6 ms, respectively, once the system (clays and tap water) reached equilibrium. For this experimental program, the peaks for KRC and IRC are very close but IRC shows amplitude peaks at slightly higher T_2 values. This is likely due to the portion of particles whose diameters are approximately 50 μm.

The total amplitude readings varied significantly while testing MRC, even though the amount of water in the system did not change. Such observations have traditionally been attributed to swelling [2]. Consequently, the weight of water as calculated from mass balance and the in-house NMR method [10] do not correlate well. In fact, percent differences between these two methods were as high as 50%. This scattering occurred almost immediately after adding distilled water, which is expected because freshwater produces maximum swelling [2]. The spectrum for MRC at equilibrium after exposure to 20wt% brine is not included in Figure 3. This is because the weight of water using the in-house NMR method was more than 50% greater than the weight of water using the mass balance method. The larger than expected amplitude for MRC is either due to signal from a portion of the interlayer water or there is more than a monolayer of water on the surface of the clay [4].

The geometric mean of T_2 (T_{2gm}) is usually another parameter used to gain information regarding solid-fluid interactions because in an air/water system, lower T_{2gm} values usually indicate that the fluid is residing in smaller pores or is more tightly bound to the particle surfaces. T_{2gm} values for the samples analysed in the program correlate closely with T_2 peak values for uni-modal spectra in Figures 2 and 3. For a given fluid and concentration, MRC consistently produced the lowest T_{2gm} values of all the clays at both equilibrium and immediately after the adding fluid. Interestingly enough, the T_{2gm} values for MRC immediately after fluid addition were the lowest at 20wt% fluid concentration and the highest at 10wt% fluid concentration. At a given concentration, IRC consistently produced higher T_{2gm} values than KRC. This may be due to the fact that IRC has larger particles than KRC so if wettability in these two samples is similar, the fluid in IRC will produce amplitude peaks at higher T_2 values than the same fluid in KRC.

CONCLUSIONS

Introducing up to 20wt% of fluid to dry clays, regardless of salinity, produces uni-modal spectra and the location of the single amplitude peak can help in determining clay type. Isolated clay samples produce amplitude peaks at T_2 values less than 10 ms. Amplitude peaks at T_2 values of approximately 1 ms denote the presence of montmorillonite while slightly higher T_2 values indicate the presence of kaolinite or illite. Scattering of total amplitude values for the same sample over time indicates montmorillonite while data that fluctuates very little may infer the presence of illite.

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Table 1. Chemical analysis of clays [5, 6]

Component	IRC	KRC	MRC
Silica	72.7	49	60.4
Alumina	15.6	33.1	17.6
Potassium oxide	2.2	0.6	0.2
Iron oxide	1.2	1.1	0.1
Titanium oxide	0.6	1.2	0.2
Magnesium oxide	0.5	0.2	6.5
Barium oxide	0.4	0	0
Calcium oxide	0.2	0.2	2.8
Sodium oxide	0.1	0.1	0.1

Table 2. NMR parameters

Parameter (units)	Value
Number of trains	16
Post-train delay (ms)	5500
Time-echo spacing (ms)	0.3
Number of echoes	5000

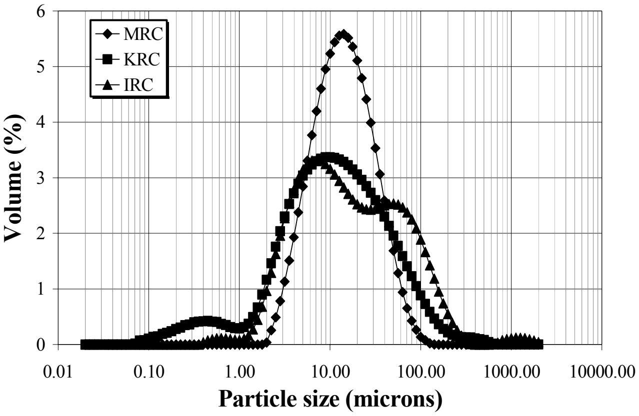

Figure 1. Particle size distributions of clay samples

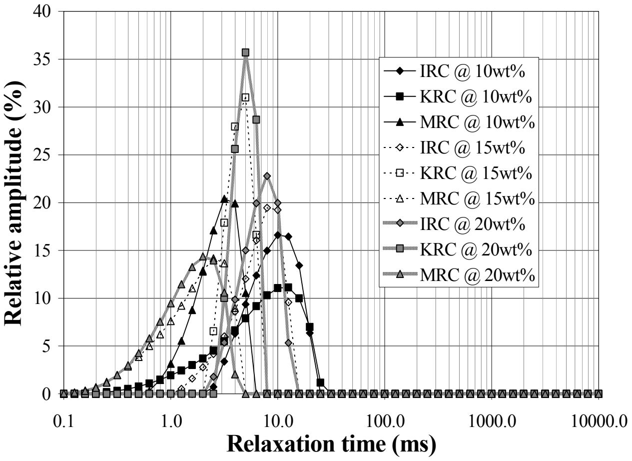

Figure 2. NMR spectra of clays immediately after adding tap water

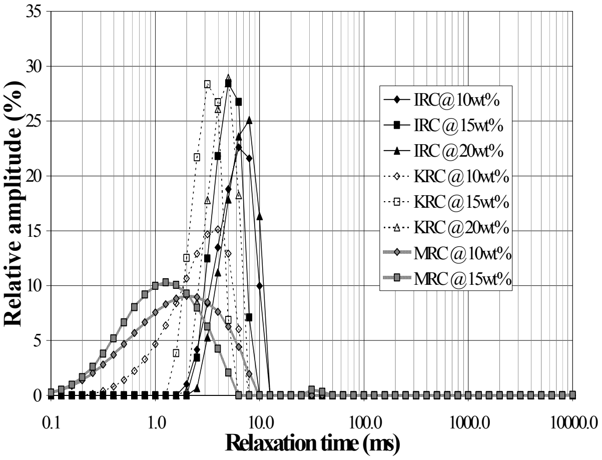

Figure 3. NMR spectra of clays at equilibrium