SCA2003-59: USING NMR SPECTRA TO DETERMINE COMPOSITIONS OF UNCONSOLIDATED SAND/CLAY/BRINE/HEAVY OIL SAMPLES

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ABSTRACT

Low field nuclear magnetic resonance (NMR) is incapable of detecting the complete signal from heavy oil and bitumen because part of the signal relaxes too quickly to be measured. In samples that are free of clays or have high water contents, the contribution from water to the NMR spectrum is distinct from heavy oil and bitumen, thus one can calculate water content and oil content is assumed to be the difference. It is more difficult to determine the oil content in partially saturated samples that also contain clay because the relaxation times of clay bound water and heavy oil and bitumen fall in the same range. Results from samples with clays, sand and low-salinity brine show that clay bound water has a characteristic response. Heavy oil was added and the differences in the NMR spectra before and after heavy oil addition were used to create a preliminary predictive algorithm for determining clay content in clay/brine suspensions and solids/brine/oil systems. This algorithm predicts oil, water and clay content and may lead to improved characterization of ores and froths as well as enhanced oils sands recovery.

INTRODUCTION

Nuclear magnetic resonance (NMR) logging tools have been used in the petroleum industry for numerous applications, such as determining porosity and permeability, characterizing heavy oil and bitumen [1, 2], determining the composition of oil/water emulsions [3] and determining heavy oil viscosity [4]. NMR logging tools obtain information regarding fluids in porous media by using magnetic fields to polarize the protons in the fluid and monitoring the time it takes the protons to return to equilibrium. This time is commonly termed the transverse relaxation time (T_2). Protons in bulk fluids such as water have a T_2 value of approximately two seconds, but the T_2 values for heavy oils and bitumen are much faster (e.g., between 1 and 10 ms). The reason for this is that the protons in heavy oil and bitumen are restricted due to the high fluid viscosity [5]. Restriction of proton movement can occur also because the fluid has sorbed onto clays or organic matter in the sample [6]. In fact, clay bound water relaxes at approximately the same time as heavy oil and bitumen (e.g., less than 10 ms) [5, 7], which makes it difficult to differentiate between the heavy oil and clay bound water signals [8]. This makes the T_2 cut-off method, commonly implemented to calculate volumes of free and bound fluid [9], impossible to use on samples with heavy oil and clay bound water because the

assumption that the signal below the T_2 cut-off value is due to heavy oil alone is incorrect. If the contribution due to clay bound water is not accounted for, estimates of reserves will be higher than the actual reserves. There have been attempts to separate oil and water signals in NMR spectra [9, 10] but these methods were not developed for samples containing heavy oil or bitumen and clay bound water. The purpose of this work is to formulate a procedure to estimate water, oil and clay content based on NMR logs that will correlate with core analysis data. Such a procedure would allow one to determine the composition of ores and froths. Advantages of using this tool over the Dean-Stark method for determining sample composition are that one obtains results more quickly and easily using NMR; only a small representative sample is required for analysis and these NMR measurements can be taken on-site without having to transfer the sample to lab facilities. This work may eventually lead to faster and improved characterization of oil sands and tailings streams.

EXPERIMENTAL
Materials
Three clays (denoted as such due to particle size and not surface chemistry), sand, low-salinity brine and heavy oil were used in this experimental program. The illite-rich clay (IRC) is mined from Ravenscrag, Saskatchewan, Canada, while the kaolinite-rich clay (KRC) is mined in Troy, Idaho, USA [11]. The montmorillonite-rich clay (MRC) was a calcium-substituted source clay from Arizona, USA [12]. The characteristics of the sand used can be found elsewhere [13]. The brine consists of 2wt% NaCl and the oil used is heavy crude from Cold Lake, Alberta, Canada. This oil has a viscosity of 50 000 mPa·s and a density of 0.9886 g/cm^3 at 30°C [4].

Instrumentation
All NMR measurements were performed at ambient temperature and pressure using the NUMAR CoreSpec 1000^{TM} at a frequency of 1 MHz and a field strength of 0.024 T. Low field NMR is more appropriate than high-field NMR for analysis of porous media because the lower field gradient minimizes the possibility of data degradation during a measurement [14]. The NMR acquisition parameters used for the suspensions and the mixtures were chosen to capture the maximum amount of information in the range of T_2 values where the fluids will likely relax. The data was processed using EchoFit v. 3.02, a software package created by NUMAR Corporation, a subsidiary of Halliburton, that employs the non-negative least squares method to create the NMR spectra.

Procedure
Three sets of clay/brine suspensions, with each set containing IRC, KRC or MRC, were tested. The clay content in each set of suspensions varied between 8 and 32wt%. The vials were tightly sealed, shaken for one minute and allowed to settle for 24 hours before NMR measurements were taken. Three sets of sand/clay mixtures were also created with 5, 10, 20, 30, 40, 50 and 100wt% (of total solids) of each clay. For easy reference, the samples with IRC were labelled I05, I10, I20, I30, I40, I50 and IRC. This system was used for labelling the samples with the other clays. The samples were shaken to ensure

that the clays were dispersed throughout the solids, then they were measured dry. Additional NMR measurements were taken 0, 1, 4 and 24 h after adding 5wt% (of total sample weight) low-salinity brine and after bringing the total heavy oil content to 4.5wt%, 8.5wt%, 16wt% and 22wt%. This measurement schedule was adopted because it was determined that water uptake in wettable samples predominantly takes place in the first 24 hours [12]. Such a schedule was not required for the suspensions as the solids were fully saturated, unlike the sand/clay mixtures that are only partially saturated.

RESULTS AND DISCUSSION

Solids/brine systems

Figure 1 shows NMR spectra of suspensions with increasing MRC content after 24 h of exposure to low-salinity brine. This figure shows the amplitude peak between 10 and 100 ms growing in size as the clay concentration increases, which is expected as this correlates to the relative contribution of clay bound water. The same figure also shows that the relative contribution to total amplitude from bulk water decreases as clay content increases, which is also expected. These characteristics were apparent in the other clay/brine suspensions. Figure 2 shows NMR spectra of sand/clay mixtures with increasing KRC content 24 h after adding low-salinity brine. This figure shows that the amplitude peaks shift to lower T_2 values with increasing clay content. This trend, which is expected because an increase in clay content causes the overall pore size distribution to shift to smaller values, has been observed in other partially saturated samples [7, 15].

Solids/brine/oil systems

The NMR spectra of wetted sand/MRC mixtures 24 h after exposure to any given oil content (not shown) bore a strong resemblance to the spectra in Figure 2 in that there was a shift of the dominant amplitude peak to lower T_2 values as clay content increased. This was true for the other sets of sand/clay mixtures and agrees with results obtained in-house from other samples that were partially wetted and then exposed to heavy oil.

Another parameter analysed was the geometric mean of T_2 (T_{2gm}) of the entire sample. This was plotted against clay content to create Figure 3. This figure shows a strong correlation between clay content and T_{2gm}, which agrees with previous findings collected in-house. The close proximity of the data points suggest that the observable trends are similar for IRC and KRC. MRC produces lower T_{2gm} values at any given clay content. This was also seen in the solids/brine systems, but the corresponding plot is not shown here. Figure 3 can be used to determine the clay content of a sample based on NMR data, regardless of whether or not heavy oil is present.

Determining sample composition from NMR data

A method was developed to determine oil and brine content based on the NMR spectra from a sample containing both fluids and is described in more detail elsewhere [2, 16]. This work has allowed us to include the calculation of clay content in a sample since clay content can be determined by using a plot such as Figure 3. The T_{2gm} of a sample can easily be calculated once the NMR data is collected.

This method was applied to the samples analysed in this experimental program and compared to the benchmarking mass balance data. A representative comparison of fluid contents based on the two different methods is shown in Figure 4. The clay content of the samples was calculated using mass balance data and the correlation equations like the ones in Figure 3 and the results from these two methods are plotted in Figure 5. The data from MRC/sand mixtures is not included in Figure 5 because the results from these samples showed considerably more scatter. The reason for this is not known at this time. However, Figure 5 shows that there is a strong correlation for clay content calculated using the two different methods when analysing illite and kaolinite.

While the methodology shows great promise, the authors do realize that additional tests are required before these nomographs can actually be implemented towards characterization of heavy oil, oil sands and tailings streams. A wider range of brine contents, oils, and clay types, contents and distributions will be tested to refine this procedure and the necessary plots.

CONCLUSIONS
The results collected led to the following conclusions:
- Water in a partially saturated sample invades a dry, water-wetting sample immediately, but there is fluid migration over 24 hours.
- An increase in clay content causes the amplitude peaks in an NMR spectrum to shift to lower relaxation times.
- Clay bound water can be distinguished even in spectra obtained from samples also containing heavy oil.
- A methodology has been developed to calculate sample composition based on NMR data.
- NMR data can be used to determine brine content in clay suspensions and samples containing clay sediments with strong correlation to mass balance calculations.
- NMR data can be used to determine clay content with strong correlation to mass balance calculations.

NOMENCLATURE
IRC   illite-rich clay
KRC   kaolinite-rich clay
MBC   mass balance calculations
MRC   montmorillonite-rich clay

NMR   nuclear magnetic resonance
T_2 transverse relaxation time, s
T_{2gm} geometric mean of T_2, s

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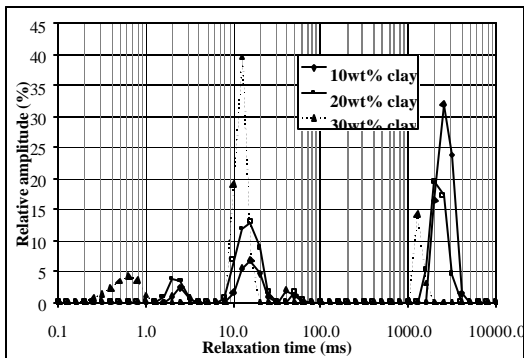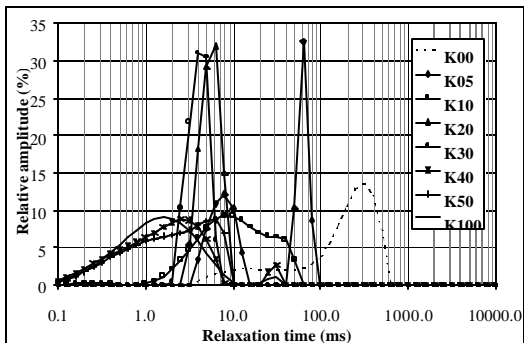
Figure 1: NMR spectra of MRC/brine suspensions.

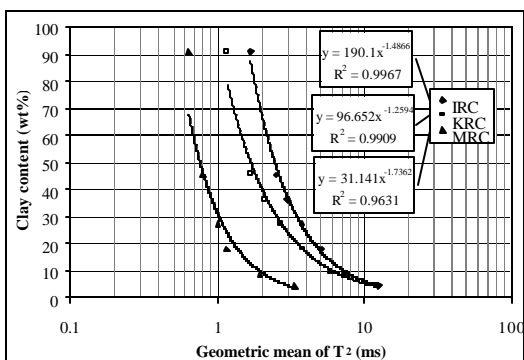**Figure 2:** NMR spectra obtained 24 h after adding brine to sand/KRC mixtures.

Figure 3: T_{2gm} values vs. clay content for wetted samples with 4.5wt% oil.
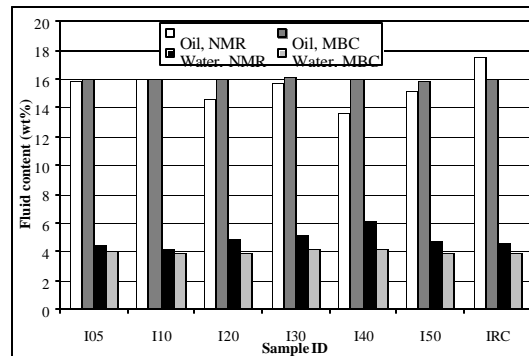

Figure 4: Fluid composition calculated using mass balance calculations (MBC) and NMR on samples with IRC and 16wt% oil.
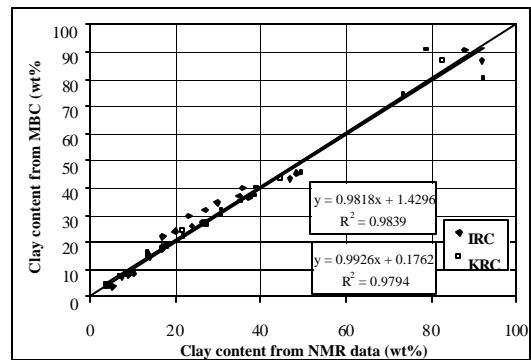

Figure 5: Clay content determined using MBC and NMR.