LOW FIELD NMR APPLICATIONS IN OIL SANDS MINING AND EXTRACTION

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ABSTRACT

Previous experience has proven that low field Nuclear Magnetic Resonance (NMR) has considerable potential for the characterization of cores containing oil, for conventional and heavy oil reservoir characterization. In oil sands mining and extraction, fast methods for determining the oil, water and solids content in ores and froths are necessary for plant process control and optimization. Currently the benchmark for such measurements is the Dean Stark extraction, which although fairly accurate is very time consuming (approx. 48 hours turnaround). In this work, NMR based methods are described for the analysis and determination of these constituent fluid and solids fractions.

The experimental procedures for NMR characterization of ores and froths consist of a single NMR measurement and a single weight measurement. The nature of the in-situ fluid signals can be inferred based on the properties of the NMR spectra and calibration parameters such as the spectra of pure fluids. A large database of ores and froths has been measured, and some very interesting observations have been made. NMR outputs are water content, bitumen content and solids content. Spectra representative of high fines content have also been identified. Predictions are compared against measured oil, water and solids fractions obtained by Dean-Stark extraction, mostly on sister samples. The results obtained to date are preliminary but have been encouraging enough to warrant further development, while plant applications have been identified. This work presents a novel application of NMR technology for an industry that can benefit considerably from fast and accurate characterization of ore and froth samples.

INTRODUCTION

The oil sands of northern Alberta contain some of the largest reserves of heavy oil and bitumen in the world. Second only to the reserves in Saudi Arabia [1], the oil sands are the future of the oil industry in this country for years to come, and will allow Canada to continue to be a world leader in both oil production and technology development. Approximately 19% of these bitumen reserves are found in unconsolidated deposits that lie close enough to the surface that they can be recovered using surface mining technology [2]. In 2003, this translated to 35% of all heavy oil and bitumen production

[1], and billions of dollars have been invested in oil sands mines. Properly predicting recoveries and process optimization is therefore of considerable value to the industry.

There are several areas in oil sands mining operations where it is important to have an idea of the oil, water and solids content of a given sample. During initial characterization of the reservoir, it is necessary to determine oil and water saturation with depth and location in the reservoir, in order to determine how the field should be mined. Later, during the processing of the mined oil sand ore, having information about the oil, water and solids content of material in the separator tanks will allow for process optimization and control. The industry standard for accurately measuring oil, water and solids content is Dean-Stark (DS) extraction. This is essentially a distillation procedure, whereby boiling solvent is used to vaporize water and separate the oil from the sand. Oil, water and solids are separated and their contents measured by mass balance. The problem with DS is that it is expensive and time consuming. Centrifuge technology is often used for faster process control, but this is highly inaccurate due to similar fluid densities. New methods for fast measurements of oil, water and solids content are needed.

In this work, low field Nuclear Magnetic Resonance (NMR) is shown to be a viable technology for performing fast, accurate and non-destructive tests for oil, water and solids content in oil sands mining samples. NMR measures the response of hydrogen-bearing fluids (oil and water) when exposed to low frequency magnetic fields. An NMR spectrum therefore contains the contribution of only the oil and water in an oil sand sample, and if the signals can be separated then they can be related to fluid content. Fluid content determination algorithms have been developed, based on observations of different fluids in porous media. Oil and water saturations are determined for both oil sand ores and froths from the hot water floatation process used for separation and recovery of the oil. Spectra properties are also identified that can be used to estimate not only fluid content, but also information regarding the processibility of samples.

NMR PROPERTIES OF OIL SAND SAMPLES
Figure 1(a) shows example NMR spectra of water in the bulk phase and in different porous media. Water has a low viscosity, meaning that its bulk relaxation rate will be slow and its relaxation time is around two seconds. If water is instead placed inside a porous medium such as sand, protons are restricted by the sand grains and additional surface relaxation is observed [3,4]. The total relaxation rate is the summation of both the bulk and surface relaxation, but for low viscosity fluids surface relaxation effects dominate inside porous media. Therefore, fluids in small pores will relax faster than fluids in large pores, and the NMR spectrum is analogous to a pore size distribution [3,4]. When the porous medium consists of clay instead of sand, the pore sizes are further reduced, leading to even faster relaxation times. Water bound to different kinds of clays can exhibit different peaks, as shown in Figure 1 (a). Oil sands contain both sand and different types of clay, thus the spectrum of water in oil sand is fairly complex.

Figure 1 (b) shows the NMR spectrum of an oil sand, and that of a bulk oil sample extracted from the oil sand. The oil is highly viscous and often referred to as bitumen. The relaxation of the bulk oil is therefore very fast, and generally occurs as a broad peak relaxing under 10 ms [5,6]. When comparing the spectrum of the oil to that of in-situ oil and water inside an oil sand ore, it can be seen that the ore also contains a corresponding broad, fast relaxing peak that occurs at approximately the same relaxation time as the bulk oil. The viscous oil is therefore relaxing at approximately the same location whether in bulk or in-situ [7], and if there were any effect of the porous medium it would be to cause additional enhanced relaxation. Therefore, any signal beyond the first peak of the oil sand ore spectrum must be only from water.

Methodology for Fluid Content Determination
The measured NMR amplitude of a given fluid can be related to its mass through the definition of amplitude index (AI):

$$AI_x = \frac{A_x}{m_x} \tag{1}$$

Where A_x = NMR amplitude of the fluid, oil (o) or water (w)
m_x = the measured mass of the fluid.

If a fluid with a known value of AI were measured and a certain amplitude were obtained, Equation 1 could then be re-arranged to determine the mass of the fluid. Previous work with bitumen-water mixtures [8-10] has shown that the signals from bitumen and water can be separated in an NMR spectrum due to their different viscosities. The oil and water amplitudes can be summed up and with their AI values known, Equation 1 can be used to determine the oil and water cut in these fluid streams. In oil sands mining samples, similar methodology can be applied to determine the oil and water fluid masses. If the signals from oil and water with known AI values can be separated and their respective total amplitudes found, then Equation 1 can be used to determine oil and water mass in these samples. If the total mass of the sample has also been measured, then fluid saturation can be determined using the following expression:

$$S_x = \frac{1}{m_s} \times \frac{A_x}{AI_x} \times 100 \tag{2}$$

Where S_x = the saturation of oil (o) or water (w)
m_s = the total mass of the sample (oil, water and solids).

The methodology for determining oil and water content in oil sands mining samples is to take a measurement of the total sample mass, and then obtain the sample NMR spectrum. The oil and water signals are separated, and their respective masses are found using Equation 1. Equation 2 is then used to calculate the fluid saturations. Unfortunately, as

can be seen in Figure 1 (b), the spectrum of an oil sand is complex, containing contributions from bulk bitumen, water in sand, water in clays, and also water in thin films around sand grains, surrounded by bitumen [11,12]. Therefore, separating the oil and water signals and relating these amplitudes to mass is not a trivial exercise.

OIL AND WATER CONTENT PREDICTIONS IN ORES

Five wells were cored in Northern Alberta. From these wells, 700 samples of ore were taken and measured in our laboratory. These samples were collected in 20 mL glass scintillation vials and frozen to prevent loss of water. NMR measurements were taken at 30°C using a Corespec 1000^{TM} low field NMR relaxometer, at an echo spacing of 0.3 ms. Inversions were made using commercial software [13], however these results should be readily transposable to other machines with similar capabilities and NNLS inversion algorithms. Sister samples of these 700 ores were also collected and sent to independent commercial laboratories for DS analyses of oil, water and solids content. 150 samples out of this database were later found to have poor signal-to-noise ratios for the NMR spectra, meaning that their spectra could not be used with as much confidence as samples with higher signal-to-noise ratios. This left 550 samples, which have been used in the development of our NMR ore prediction models. Fluid mass predictions using this same database of samples has also been published elsewhere [14].

An examination of Figure 1 (b) shows that the bulk oil NMR peak is in roughly the same location as the first peak in the oil sand ore spectrum. The explanation for this is that the highly viscous oil is relaxing so quickly through bulk relaxation that its relaxation is essentially independent of the porous medium [7]. Therefore, it may seem reasonable to assume that the entire signal in the first peak can be assigned to bitumen, while any signal beyond this peak is water. From the database of 550 samples, 85% of samples showed a distinct, fast relaxing peak similar to the spectrum in Figure 1 (b). Therefore, as an initial attempt the spectra of the samples were separated at the local minimum indicating the end of the first peak. Water amplitudes were summed and divided by the AI value for water, which is a known constant in any given NMR machine. Water saturation was calculated and is compared against DS water saturation in Figure 2.

The majority of the samples in Figure 2 show DS water saturation that is higher than the NMR estimate. This means that there must also be some signal from water hidden in the first peak of the ore spectra, and excluding this water leads to low estimates of water saturation. Figure 1 (a) verifies this conclusion; when there are clays present, the water signal occurs below 10 ms, overlapping with the first peak of the ore spectrum. To account for this water, a simple peak de-convolution was applied to the first peak of the ore spectra that separates the peak into two contributions: that of oil and water. Details of the de-convolution algorithm are provided elsewhere [7,15]. Essentially, second derivatives are calculated to find the inflection point that indicates the first peak is beginning to taper off. Oil is taken to be the entire amplitude up to this point, and decreases linearly to zero beyond the inflection.

Figure 3 shows the results for two ore samples that have distinct first peaks. The algorithm works well in situations where the first peak ends cleanly below 10 ms, as in Figure 3 (a), and where there is more significant overlap with subsequent peaks, as in Figure 3 (b). With this approach, even when the first local minimum is not found until later values of T_2 (above 10 ms), an oil peak can still be determined. The initial attempt (Figure 2) calculated the signal all the way up to the first local minimum to be oil, meaning that the NMR estimate of water content would be significantly lower.

45 samples, or 8% of the database, had spectra that do not have a distinct, fast relaxing first peak. An example of one such spectrum is found in Figure 4 (a). These samples are characterized by having the skewed first peak with the first local maximum occurring at a T_2 value greater than 2 ms. However, the proposed oil peak de-convolution algorithm could locate an inflection point before the maximum, and calculate the oil as with the other samples. Finally, 30 samples, or 5% of the database, had a first peak that had no inflection point before the local maximum, as in Figure 4 (b). More sophisticated de-convolution algorithms are being developed for these samples, but it was determined manually that if the signal up to 2 ms were simply taken to be oil and all signal above this cutoff was water, the NMR water matches well with DS measurements.

Oil and water amplitudes were determined using this approach for all 550 ore samples. The remaining step in calculating saturation is to determine the fluid AI, which is needed to convert the de-convoluted amplitude into fluid mass. As mentioned previously, the AI value of water is a known constant in any given machine, making the translation of water amplitude to mass and saturation simple. Oil, on the other hand, can vary significantly from sample to sample due to differences in the physical and chemical makeup of the oil. In previous work, however, it has been observed that oil AI can be related to the oil geometric mean relaxation time [7,15] since both vary monotonically with oil viscosity. Therefore, the de-convoluted oil average relaxation times were calculated and related to oil AI through the following empirical correlation [14]:

$$\text{RHI} = -0.3731\left(T_{2\text{gm}}\right)^2 + 1.1751\left(T_{2\text{gm}}\right) \tag{3}$$

Where RHI = oil AI divided by water AI at the same temperature
        $T_{2\text{gm}}$ = geometric mean oil relaxation time.

Since RHI normalizes the oil AI value to water, the correlation can be used to estimate oil AI independent of the NMR machine used to generate the data. It should be noted that this correlation was developed based on froth de-convolutions [13], since these spectra all had clear and distinct first peaks with very little overlap at the end of these first peaks. An ore RHI correlation was also developed using the samples in the ore database [13], however there was significantly more scatter in the ores due to varying degrees of overlap between oil and clay-bound water. Therefore, the froth RHI correlation was better defined and using the same correlation for ores and froths did not introduce any

additional error in the bitumen saturation predictions. Using this correlation, the oil RHI and hence its AI value can be calculated, and oil mass and saturation can then be found.

There were also several samples where the de-convolution algorithm predicted small amplitude oil peaks with very low T_{2gm} values, outside of the range of samples used to generate the correlation. These samples had very little oil, however Equation 3 would predict a very small value of RHI, which would lead to an exaggerated estimate of oil mass. Therefore, whenever the predicted RHI value was less than 0.3, which was outside the range of the empirical correlation, RHI would then be automatically set to an average value of 0.4 in order to have reasonable oil mass predictions.

Figure 5 shows the NMR water and oil saturation predictions, plotted against the measured DS values obtained for sister samples. The average error in the water saturation predictions is only 0.92%, with a standard deviation of 0.72% and a maximum error of 4.23%. For bitumen, the average error in saturation is 1.04%, with a standard deviation of 0.95% and a maximum error of 6.46%. For fluid saturation predictions required for initial reservoir characterization or monitoring of the quality of the recovered ore from day to day, the NMR predictions are accurate.

OIL AND WATER CONTENT PREDICTIONS IN FROTHS

In oil sands mining, bitumen is separated from the water and sand using variations of the Clarks hot water floatation process [11]. In general, the ore is first conditioned by slurrying with water to initiate the separation of the oil from the sand. Additional hot water is later added to the slurry, and the resulting mixture is allowed to separate by gravity. The froth obtained from the top of the separation tanks consists of a much higher relative fraction of oil and water, and a lower solids fraction than the original ore.

Figure 6 shows an example of oil sand ore sample and its associated froth. The amplitude of the first peak is larger in the froth, showing that the oil content in froths is higher than in the ores. There is also significantly more amplitude beyond the first peak, indicating that the water fraction is also higher than in the ores, which is also expected based on the physical characteristics ores and froths. The froth also has a mass of only 21.6 g, compared to 35.5 g for the ore. The fact that the froth contains more amplitude for a smaller total mass of sample indicates that the solids fraction in froths is significantly lower than in ores. The distribution of water peaks is also much wider than for the ores, indicating a more physically complex system. There is still water bound to remaining solids in the froths, however water is also present as a bulk phase, and in emulsion with the oil and any air in the system. Despite these differences, for oil and water content estimation the same algorithm can be applied as for the ores.

The froth database consists of 49 samples from the same area as the ores [14]. The samples were once again measured in 20 mL glass scintillation vials at 30°C, using the same NMR relaxometer at an echo spacing of 0.3 ms. The average sample mass of the froth samples is 22 g, as opposed to an average mass of 38 g for the ores, which is

another indication that the solids content is lower in the froths. The same de-convolution approach was applied as for the froths, and the RHI correlation shown in Equation 3 was applied. Figure 7 shows the NMR water and oil saturations, plotted against the DS values. The average error in the water saturation predictions is 1.86%, with a standard deviation of 1.27% and a maximum error of 4.56%. For the oil predictions, the average error is 3.00%, with a standard deviation of 2.02% and a maximum error of 10.09%. It should be noted, however, that although the errors in the froth predictions appear to be larger than for the ores, the actual mass predictions were similar [14]. The larger errors in saturation are due to the fact that the froths have less mass than the ores, and that the ore database is larger.

The information gathered in an NMR measurement is the total sample mass and the NMR estimates of oil and water content. Solids content can then be determined by subtracting the fluid content from the total sample mass. Figure 8 shows the solids content by difference plotted against DS solids content. So long as the NMR oil and water content predictions are accurate, the solids fraction in a given froth sample can also be determined. This leads to improved process control in frothing operations.

INSIGHTS INTO ORE AND FROTH PROCESSIBILITY

Several ore samples were measured that were defined in terms of their "grade", or processibility. This term refers to the ability of the ores to undergo good separation of oil from water and solids during frothing. Figure 9 (a) is an example of a high grade sample, meaning that the oil will separate well under normal frothing operations. This spectrum has a clean, distinct fast relaxing peak with a local maximum before 2 ms. Figure 9 (b), on the other hand, has significantly more overlap between the oil and bound water signals. This type of spectrum is similar to Figures 3 (b) or 4 (a), where the first peak does not have such a distinct ending. The higher degree of overlap hints at a larger contribution from bound water, which would be present in a sample containing more clay or fine particles that would hinder separation.

Figure 10 (a) is a spectrum of a low grade, or poorly processing, ore. This ore, when frothed, would not undergo good separation of the oil from the solids and water, meaning that recovery from this ore would be lower. As can be seen, this spectrum has similar properties to those of Figure 4 (b), where the first peak appears skewed with a local maximum occurring above 2 ms and no inflection point before the local maximum. This first peak cannot be easily resolved into oil and bound water amplitude. Figure 10 (b) is a synthetic sample containing 4.5% bitumen and 4.5% water, and 91% solids consisting of equal masses of sand and clay. This significant clay fraction leads to a first peak that is similar to that of Figure 10 (a), which hints that processibility can be related to the overlap and fraction of bound water in the first peak. NMR spectra can therefore be used not only for fluid content predictions, but also to provide an indication of the recovery or frothing potential of different samples of oil sand.

CONCLUSIONS

Low field NMR spectra can be a useful tool for estimating the oil and water saturation of oil sand ore and froth samples. NMR measurements, which are non-destructive and simple to perform, correlate well with measured values of oil and water content over a wide range of fluid saturations. Despite the simplicity of the NMR models, estimates are accurate enough that they can be used for reserves estimation and process control. The same de-convolution algorithm can be used for both ores and froths, and similar errors are observed in both types of samples. In addition to fluid content predictions, the degree of overlap between oil and water, and the location of the first peak in the NMR spectra, can potentially be used to provide an indication of the degree of recovery that can be expected in different oil sand samples.

ACKNOWLEDGEMENTS

NOMENCLATURE

A_x	NMR amplitude of the fluid being measured, oil (o) or water (w)
AI	Amplitude index: the NMR amplitude per unit mass of fluid
DS	Dean-Stark
m_x	Mass of fluid, oil (o) or water (w), g
m_s	Measured sample mass (oil, water and solids)
NMR	Nuclear magnetic resonance
RHI	Relative hydrogen index: oil AI divided by water AI
S_x	Fluid saturation, oil (o) or water (w), %
T_2	Transverse relaxation time of a fluid, ms
T_{2gm}	Geometric mean oil relaxation time, ms

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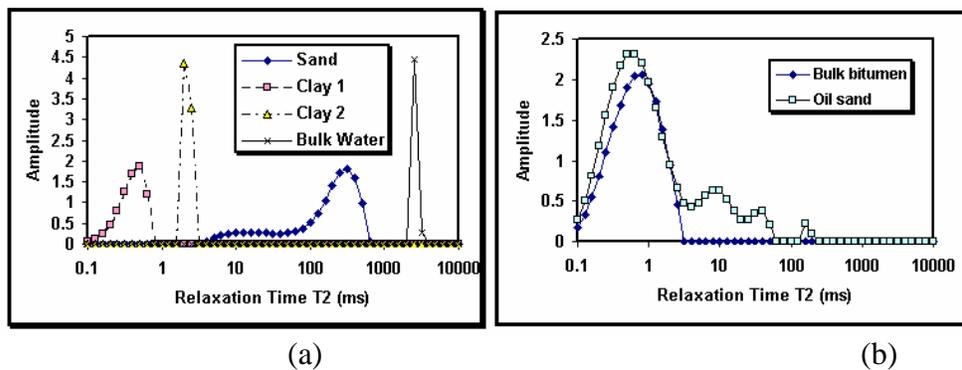(a)   (b)

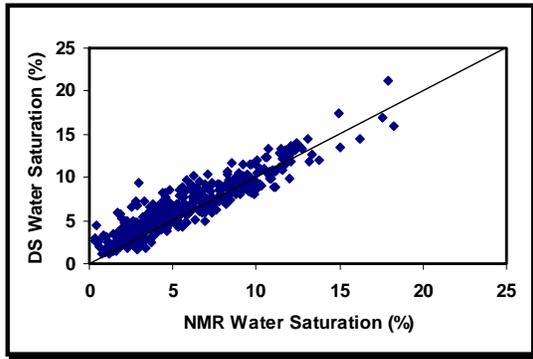Figure 1. Representative spectra of bulk fluids and fluids in porous media
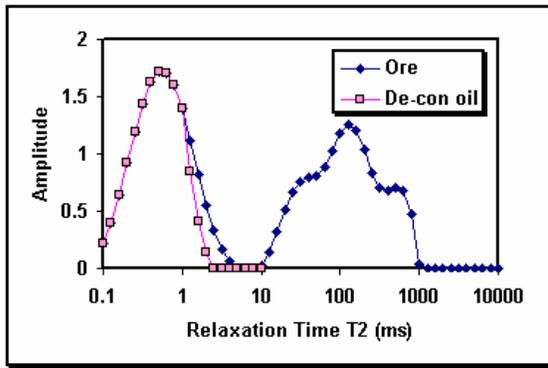
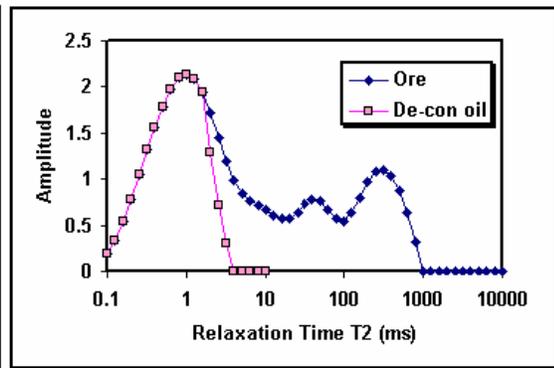Figure 2. Samples with distinct 1st peaks – assuming all the 1st peak is bitumen

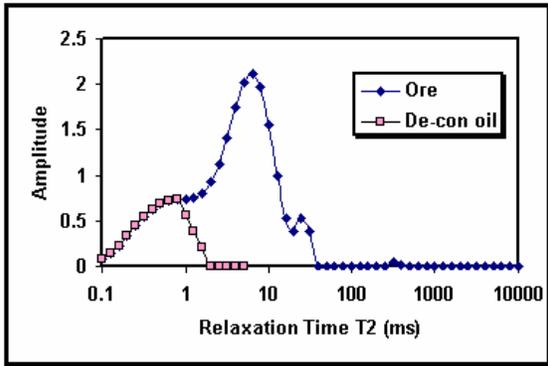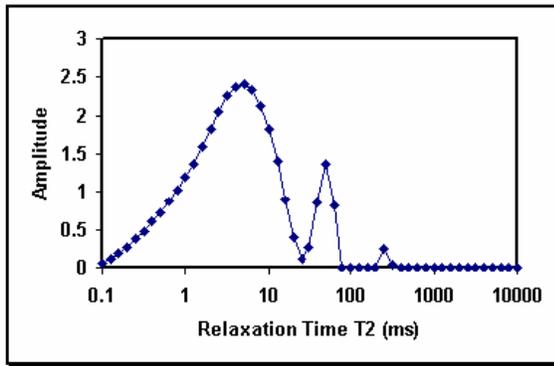(a)   (b)

Figure 3. Ores with Distinct first peaks – proposed oil de-convolution

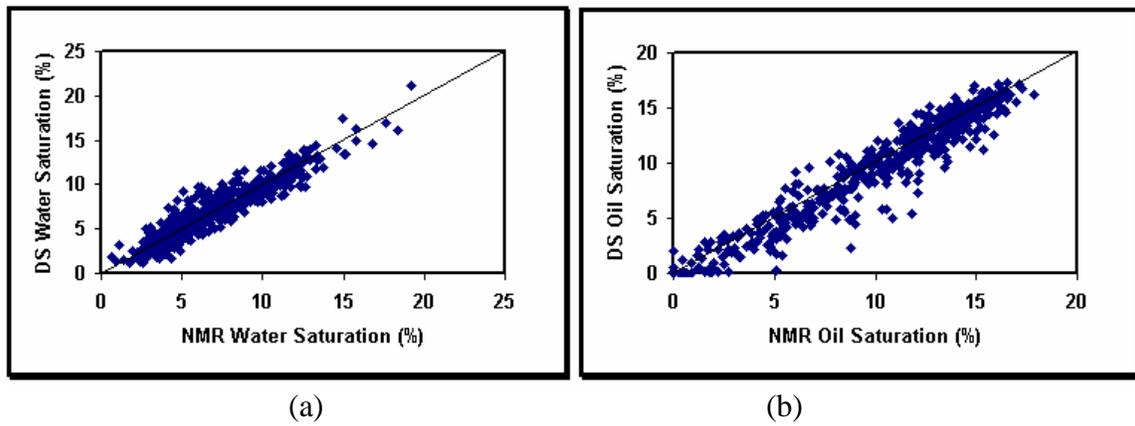(a)   (b)

Figure 4. Spectra without distinct first peaks
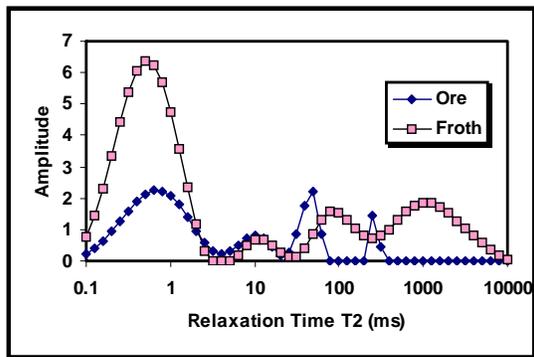
(a)   (b)

Figure 5. NMR fluid saturation after oil peak de-convolution
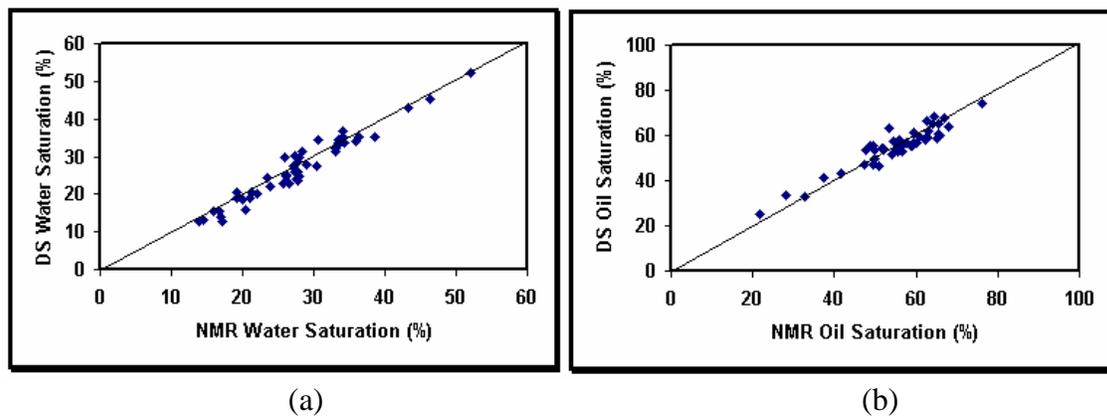

Figure 6. Sample ore and froth spectra

(a)   (b)
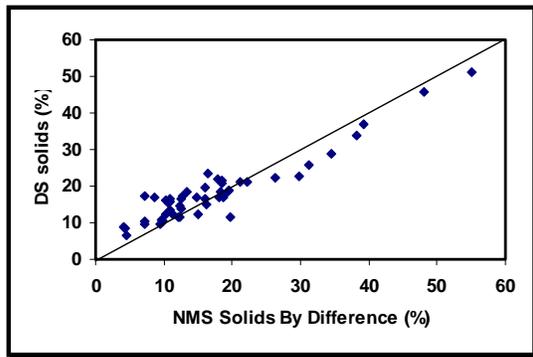
Figure 7. Froth water and oil saturation predictions
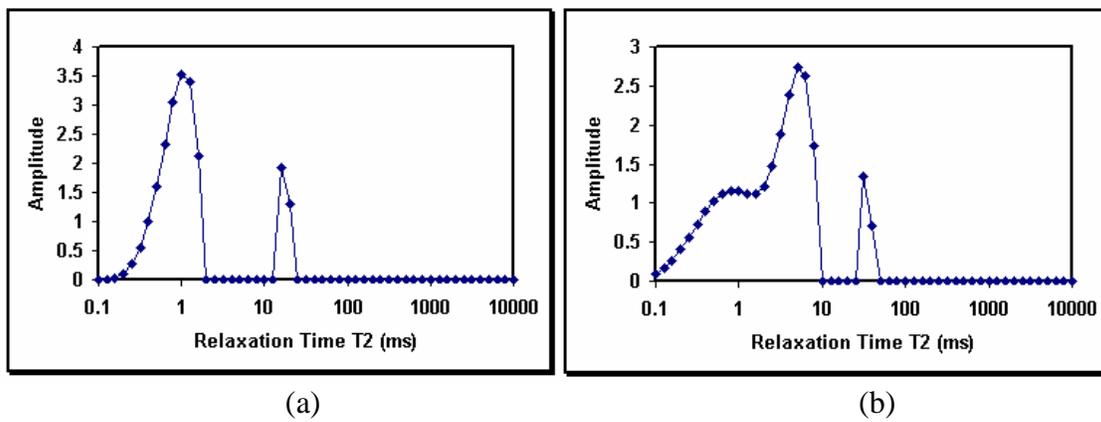
Figure 8. Froth solids content predictions

(a)   (b)

Figure 9. High and medium grade ore samples

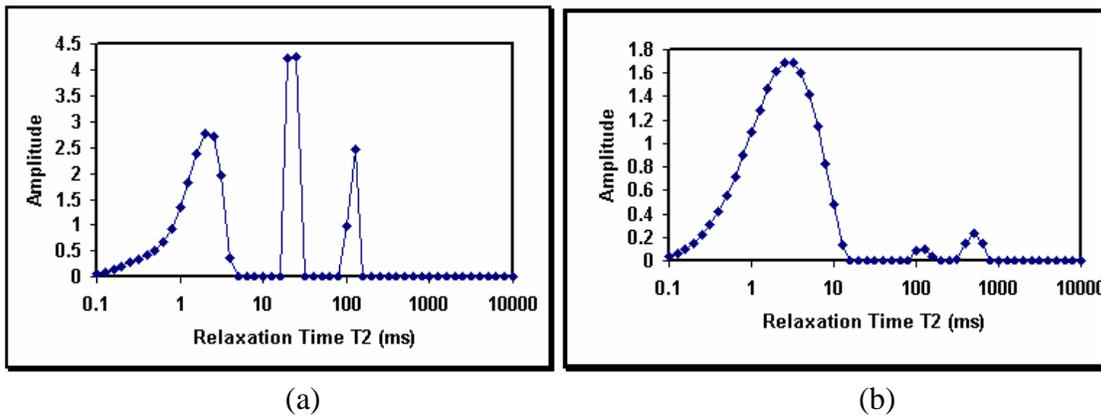(a)   (b)

Figure 10. Low grade ore and synthetic sample containing significant clay