Characterization of Oil Sands Tailings using Nuclear Magnetic Resonance (NMR) Technique

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Abstract

In the oil sands mining industry in Alberta, Canada, large volumes of tailings are produced as waste from the recovery of bitumen. This study uses the Nuclear Magnetic Resonance (NMR) technique to characterize tailings samples and their settling behaviour in presence of flocculant. An estimation of the water, oil and solids content and the variations in the settling rate are analyzed over time. NMR is used to establish if flocculant addition is successful in breaking down suspensions, or if additional chemical is required. The results show the NMR technique can be a potential on-site fast measurement of tailings settling characteristics for determining process modifications.

Key words: tailings, oil sands, settling, NMR.

Introduct

Tailings management and water recycling are important process and environmental issues in the sustainability of the Canadian oil sands industry, since the production of one barrel of synthetic crude oil (SCO) generates 1.8 tonnes of solid tailings and requires 2 m^3 of processed water (75% coming from recycled process water) . Tailings are composed principally of water (58-62%), solids (sand and clays, 37%) and a small amount (1-5%) of recovered bitumen (Masliyah 2007). This mixture is disposed to tailings ponds, where sand settles faster than clays and complete settling of stable clay suspensions can take hundreds of years. The enhancement of tailings settling rates plays a key role in water recovery and its recirculation in the oil sands extraction process. Currently, the paste technology and the consolidated tailings (CT) process are the two most common methods used in the oil sands industry to improve the tailings settling rates. The paste technology uses polyacrylamides of high density as flocculants, while the CT process uses gypsum as a coagulant. Both substances modify the interaction forces responsible for holding particles together, leading to faster solids settling and correspondingly improved recovery of clean process water (Xu 1999).

In this study, the Nuclear Magnetic Resonance (NMR) technique is used to analyze the settling characteristics of real tailings samples in the presence of different concentrations of flocculant. NMR is a non-destructive technique that uses magnetic fields to polarize the protons in a fluid (oil and water), and monitors the time it takes for these protons to return to equilibrium. This time is denoted as transverse relaxation time (T_2), which is characteristic for each substance. The result of each measurement is a spectrum showing the amplitude and relaxation time as a function of the quality and quantity of fluids analyzed (Coates 1999). In this work, the settling characteristics of tailings are studied through changes in the NMR spectra over time. The NMR results are compared against those obtained by Shell Canada using settling columns, which is the typical method used in the industry to study tailings settling rates. In general, the results show that the NMR technique can be used to verify the effectiveness of the flocculant and to establish if it is necessary to add a larger proportion of chemical to improve water release. Therefore, NMR technology can be considered as a possible online application to estimate the lifetime of tailings ponds and to monitor oil sands processing.

Methods

Six fine tailing samples are prepared by Shell Canada Calgary Research Center using a Batch Extraction Unit (BEU) at a temperature of approximately 40°C simulating a low, mid, and high-grade ore extraction. The grade is defined by the amount of bitumen recovered in the BEU process. The BEU is a low-shear laboratory approximation of the commercial Clark hot water extraction (CHWE) process. A commercial anionic acrylamide copolymer flocculant is also provided by Shell Canada. The settling of three samples is analyzed in settling columns after adding only 100 ppm of flocculant.

The team of Shell Canada performs these experiments. The other three sister tailings samples (1, 2 and 3) are provided to perform settling analysis using the NMR technique. All samples are measured in an Ecotek FT NMR tool, which operates at a frequency of approximately 1 MHz. Samples were measured using a bimodal compositional detection method. During the entire time required for sample preparation and chemical addition, the samples are agitated and maintained at 40°C. Each one of the tailings samples (1, 2 and 3) is divided in three sub-samples; therefore, 12 samples are measured in total. The first sub-sample of each group is dosed with 100 ppm of flocculant solution. Subsequently, this concentration is increased to 150 ppm and finally to 200 ppm. All the samples, including the three original tailings, are measured in the NMR tool at 0, 2, 4, 6, 24, 48 hours, one week and 3 months

Data Analysis

The two NMR values used to analyze the settling characteristics of fine tailings are the amplitude index (AI) and the geometric mean relaxation time (T_{2gm}). The amplitude index is defined as *AI = Total Amplitude / Mass*; through this definition the oil and water masses are calculated. Once AI values for oil and water are known, then in an unknown sample if the oil and water amplitudes are measured, they can be converted into fluid masses using the AI expression. The T_{2gm} value of water provides information about the solid-fluid interaction and the solids type present in a sample, since water alone is a slow-relaxing fluid, and decreases in the water relaxation times are a reflection of water associated with higher surface area solids, such as clays (Coates, 1999). The geometric mean relaxation time is defined as $T_{2gm} = \exp\left[\sum \ln(T_{2i}) A_i \big/ A_T\right]$, where, T_{2i} is the i^{th} transverse relaxation time constant, A_i is the amplitude value for each i^{th} transverse relaxation time and A_t is the cumulative total of the signal amplitude.

As previously mentioned, all tailings samples are measured in the NMR tool using a bimodal compositional detection method over a 15 minute period. This method consists of using different parameters to detect water and oil signal separately. The difference of these parameters benefits the accuracy in the water and oil mass predictions. The NMR spectra obtained using the parameters to detect the water signal are analyzed based on two cut offs: the first cut off corresponds to the area from 6 to 599 ms, and the second cut off covers the area from 600 to 10000 ms. The first region of the spectra represents the water associated with the clay fraction, and the second region corresponds to bulk or free water. Figure 1 shows the NMR spectra of a tailings sample in the presence of different flocculant concentrations. The water amplitude and T_{2gm} values are calculated for all spectra, for each region divided by the cut off points. The settling behavior analyses are based on the amplitude values and the relaxation times of the bulk water peaks and the clays bound with water peaks.

Results and Discussion

Table 1 shows the total water amplitudes, the bulk water amplitudes and the T_{2gm} values for the three original tailings samples (1, 2 and 3). Only one peak at different relaxation times is observed in the NMR spectra for the original mixtures: samples 1 and 3 have fast relaxing times, while sample No. 2 relaxes much more slowly. Based on the amplitude values, it is apparent that that sample No. 2 contains the highest water proportion, followed by sample No.3 and No.1. Additionally, sample No. 2 is the only sample with a bulk water peak, indicating that this tailings sample has considerably fewer fine solids than the other two samples. This is shown also in the higher T_{2gm} value for sample No. 2, followed by sample No. 3 and No. 1. From the T_{2gm} values alone, it is expected that samples No. 1 and No. 3 will require more flocculant addition to enhance separation.

There was no detectable oil signal in the NMR spectra of the 3 samples even using parameters to detect oil. This means that although the samples may contain oil, its amount is under NMR detection limits, which is approximately 0.7%. If oil amplitude could be measured, this would be indicative of the tailings having much oil, and thus the samples could be re-circulated through the extraction process to recover additional oil. In these samples, the NMR analysis shows that the oil content is low, so only the settling characteristics need to be optimized for water recovery.

Figure 1 shows the NMR spectra of sample No. 1 in presence of different concentrations of flocculant (100, 150 and 200 ppm) after 2 hours. According to the amplitude values of the bulk water peaks, the most effective flocculant dose corresponds to 100 ppm, followed by 200 ppm and 150 ppm. This effectiveness can be also observed by the relative size of the peaks in the bulk vs. bound water regions of the spectra. A larger bulk water peak and a smaller surface peak indicate good settling and water release.

The bulk water amplitude fractions for the three samples as a function of flocculant addition are shown in Table 2. The results for sample No. 2 show the most effective flocculant dose to be 100 ppm, followed by 150 and 200 ppm. In this case, the amplitude values of the bulk water peaks are very similar for all flocculant concentrations. This phenomenon indicates that the addition of a concentration of flocculant higher than 100 ppm is not required to accelerate water release, which can be attributed to the fact that water trapped in the clay fraction or small pores is minimal even in the original samples, as evidenced by the initial high water T_{2gm} value without flocculant addition.

In the case of the sample No. 3, the order of effectiveness of the flocculant dose is 150, 200 and 100 ppm. However, the bulk water peaks are formed at around 1000 ms only after one week. Also, the results for clay bound with water show a large peak at approximately 60 ms, which indicates that flocculant alone is not very effective for facilitating water separation in this sample. With flocculant addition water can eventually be recovered for recycling, but for improved process control the lack of the free water peak at early times (e.g. two hours after flocculant addition) would be indicative of the need for further chemical addition to facilitate faster solids settling.

Figure 2 shows the amplitude values of the bulk water peaks for the sample No. 1 during one week. The largest water release occurs in the first six hours, showing that the flocculant acts quickly and efficiently as a modifier of the interaction forces responsible for holding particles together. After this time, the amplitude values start to decrease and by one week the values are constant: even after 3 months, the bulk water amplitudes are essentially unchanged. The small changes observed in the amplitude values are attributed to evaporation effects.

In order to verify the accuracy of the NMR tool in the oil and water mass predictions, all samples are placed in an oven at 110°C for 24 hours to evaporate the remaining water. Table 3 shows the difference between the NMR and the real water and solids mass predictions for the original tailings sample No. 1 and for its sub-samples mixed with different flocculant concentrations. In this measurement technique, the water content was measured by NMR while the solids were determined by mass balance. For the sample sizes used in this study (approximately 20 g), the average absolute error in the water and solids mass predictions is 0.16.

Finally, NMR settling results are compared against the data obtained by Shell Canada using sedimentation columns after 24 hours. This method confirms that sample No. 2 presents the lowest solid content in the aqueous phase of the three samples, followed by sample No. 1 and No. 3. The Dean Stark analysis performed by Shell on the original oil sands shows that sample No. 2 contains the highest oil content of the three samples, which is usually expected from a sample with a small amount of fine solids. In the same manner, both the settling columns and the NMR verify that sample No. 3 requires the addition of another chemical agent such as a coagulant, since the percentage of solids found in overflow from the settling column at 24 hours (w/w) is larger than 0.5, and likewise the NMR bulk water fraction is also low. These results show that the NMR can quickly identify both the relative oil content and the settling characteristics of a sample.

Conclusions

The NMR technique can be used in the analysis of the settling characteristics of real tailings samples, to provide fast results that are similar to those obtained using settling columns, which is the typical method used in the oil sands mining industry to analyze tailings settling rates. The NMR amplitude values and the T_{2gm} values obtained for three real tailings samples allow for a determination of which sample contains higher clay or water content, and if another chemical agent must be added to improve the effectiveness of flocculant in the water releasing process. This study indicates that the NMR technique can be considered as a potential online application in the tailings disposition process and in the improvement of water recovery to increase the efficiency of the oil sands mining process.

Table 1 *Amplitude and T_{2gm} values for the original three tailings samples*

Sample No.	Total Amplitude	Bulk Water Amplitude	Total T_{2gm}
1	1.469	0	77.634
2	2.950	2.342	601.696
3	2.663	0	126.773

Table 2 *Bulk water amplitude fractions for varying flocculant addition*

Sample No.	100 ppm	150 ppm	200 ppm
1	0.856	0.501	0.745
2	0.977	0.974	0.976
3	0.000	0.000	0.000

Table 3 *NMR water and solids mass predictions vs real water and solids content*

Sample 1 + ppm flocculant	Original sample	100 ppm	150 ppm	200 ppm
NMR water cont.	9.959	20.791	19.235	20.051
Real water cont	9.830	20.920	19.040	19.870
Absolute error (g)	0.129	0.129	0.195	0.181
NMR solids cont.	0.681	2.086	4.875	2.469
Real solids cont	0.810	1.957	5.070	2.650
Absolute error (g)	0.129	0.129	0.195	0.181

Figure 1 *NMR Spectra of sample No. 1 mixed with different amounts of flocculant at 2 hours*

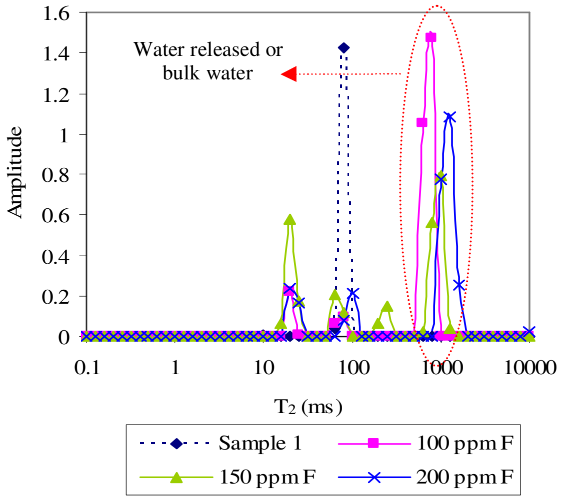
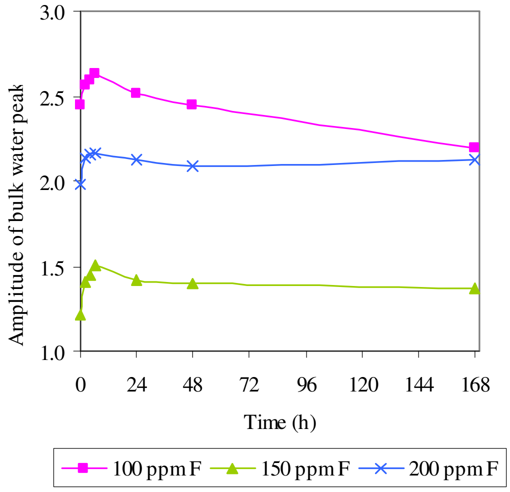


Figure 2 *Amplitude of bulk water peaks vs time (h) for sample No. 1 mixed with different amounts of flocculant*



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References

Coates G, Xiao L, and Prammer M, (1999) NMR Logging Principles and Applications, Halliburton Energy Services,Houston, TX USA.

Masliyah J.H, (2007) Oil Sands Extraction and Upgrading. Department of Chemicals and Materials Engineering, University of Alberta, Edmonton, AB, Canada, 11 B6-1-B6-48

Xu Y, Cymerman G. (1999) Flocculation of fine oil sand tails, Polymers in Mineral Processing. Edmonton, Alberta, Canada, Canadian Institute of Mining, Metallurgy and Petroleum 591: 604