UNIVERSITY OF CALGARY

Characterization of Oil Sands Tailings Using
Low Field Nuclear Magnetic Resonance (NMR) Technique

by

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Dedication

Gracias a ti por prestarme siempre tus maravillosos lentes rosados
Gracias a ti por seguir queriendo estar
Gracias a ti por estar siempre en mis más lindos recuerdos
Gracias a ti por ser mi par mejorado
Gracias a ti por mostrarme tu lado amoroso
Gracias a ti por enseñarme que siempre puedo aprender
Gracias a ti por ser mis hermosas alas
Gracias a ti por seguir a mi lado entendiendo amaneceres y atardeceres
Abstract

The oil sands mining and extraction processes in Canada produce large volumes of tailings that are a mixture of mainly water, clay, sand, chemicals and bitumen. This mixture is transported to tailings ponds, where gravity segregation occurs. During this process, a stable suspension called mature fine tailings (MFT) is formed, which requires many years to fully consolidate. Therefore, land reclamation and water recirculation become significant environmental issues. For this reason, it is important to understand the tailings content and their settling properties.

This study uses the low field Nuclear Magnetic Resonance (NMR) technique to estimate the composition of tailings samples, through a bimodal compositional detection method. Tailings settling characteristics were also studied in the absence and presence of the typical chemical substances used in the industry to accelerate settling.

The results show that the NMR technique can be a potential on-site fast measurement of composition and settling characteristics of tailings.
Acknowledgements

I would like to express my gratitude to my supervisor Dr. Apostolos Kantzas for all his support during the development of my Master’s degree.

I would also like to acknowledge the contributions of the staff at the Tomographic Imaging and Porous Media (TIPM) Laboratory, especially to my friend Jonathan Bryan and Sergey Kryuchkov.

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The collaboration of Dr. Pedro Pereira and Dr. Harvey Yarranton from the University of Calgary is also appreciated.

Finally, I would like to acknowledge the Canada Research Chair in Energy and Imaging affiliates (Shell, Nexen, Devon, PetroCanada, Canadian Natural, ET Energy, Suncor, Schlumberger, Laricina, Paramount, CMG Foundation and ConocoPhillips) and the Natural Sciences and Engineering Research Council of Canada (NSERC) for funding this research.
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<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>AEUB</td>
<td>Alberta Energy and Utilities Board</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscope</td>
</tr>
<tr>
<td>BEU</td>
<td>Batch Extraction Unit</td>
</tr>
<tr>
<td>CAPP</td>
<td>Canadian Association of Petroleum Producers</td>
</tr>
<tr>
<td>CHWP</td>
<td>Clark Hot Water Extraction Process</td>
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<tr>
<td>CPMG</td>
<td>Carr-Purcell-Meiboom-Gill Pulse Sequence</td>
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<tr>
<td>CT</td>
<td>Consolidated Tailings</td>
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<tr>
<td>DS</td>
<td>Dean Stark Extraction Method</td>
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<td>Mature Fine Tailings</td>
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<td>Sodium Hydroxide</td>
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<td>NMR</td>
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<td>NNLS</td>
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<td>NSERC</td>
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<td>TIPM</td>
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<td>AI</td>
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<tr>
<td>( m_{\text{fluid}} )</td>
<td>Mass of a fluid, g</td>
</tr>
<tr>
<td>O</td>
<td>Oil or bitumen</td>
</tr>
<tr>
<td>S</td>
<td>Solids</td>
</tr>
<tr>
<td>S/V</td>
<td>Surface area to volume ratio, ( \text{l/mm} )</td>
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<tr>
<td>TE</td>
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<tr>
<td>( T_1 )</td>
<td>Longitudinal relaxation time, s</td>
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<td>( T_{2i} )</td>
<td>The ( i )th component of transverse relaxation component, s</td>
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<td>( T_{2s} )</td>
<td>Decay time for the fluid on the surface of the porous media, s</td>
</tr>
<tr>
<td>t</td>
<td>Time, s</td>
</tr>
<tr>
<td>W</td>
<td>Water or brine</td>
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<td>( \gamma )</td>
<td>Gyromagnetic ratio, ( \text{Hz/T} )</td>
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<tr>
<td>( \rho )</td>
<td>Surface relaxivity, ( \text{mm/s} )</td>
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<td>( \tau )</td>
<td>Half of TE, s</td>
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<td>( \pi )</td>
<td>Constant, 3.14159</td>
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CHAPTER 1: INTRODUCTION

1.1 Statement of Problem

The oil sands deposits in northern Alberta in Canada contain approximately 2.5 trillion barrels of bitumen and production is expected to reach one million barrels of bitumen per day by 2010 (AEUB, 2005). The deposits are distributed among three different locations: Athabasca, Peace River and Cold Lake. The largest deposit is located in Athabasca and has the most concentrated oil sands development. These deposits are mainly recovered through surface mining technology; in 2006 alone, surface mining accounted for 82% of the total production from the Athabasca region, and 61% of the gross bitumen production from all three deposits (AEUB, 2007).

Billions of dollars have already been spent in these areas, and significant oil sands mining reserves have been identified and are being aggressively targeted by several major production companies. While these operations have provided significant economic benefits to the country, the immense size of mining projects has also led to major environmental concerns because the production of one barrel of oil requires that two tonnes of oil sand be mined, moved and processed. From these operations, approximately 75% of the bitumen is recovered; after the oil has been extracted the remaining processed sand and some water is returned to the mine site in order to reclaim the land (Masliyah, 2007).

The current process used to extract bitumen from oil sands is known as the Clark Hot Water Extraction Process (CHWP), which fundamentally consists of adding hot water to oil sands to form a sand/fluid suspension or a slurry. In this suspension, the higher density solids settle through gravity, and air is sparged into the slurry to separate the bitumen from the water. As a result, oil is recovered through flotation and can then later be upgraded into synthetic crude oil (SCO). The remaining waste product of the slurry is known as tailings, which are composed mainly of water (58 - 62%), a small amount of
unrecovered bitumen (1 - 5%) and solids (sand and clays, 37%). The solids are constituted of 95% clays and 5% sand. The three main clays contained in the clay fraction are kaolinite, illite and sodium montmorillonite (Mikula, 1996).

The management of tailings is an important environmental concern, because the production of one barrel of synthetic crude oil requires 2 m$^3$ of processed water (75% coming from recycled process water) and produces 1.8 tonnes of solid tailings that are discharged into tailings ponds. In this manner, the tailings ponds require more volume than the original oil sand, and as mining operations progress the size of these disposal ponds can become significant. In these ponds, sand settles faster than fine clay solids, which form stable suspensions that require thousand of years to reach full consolidation without the help of chemical additives. One of the causes of the slow settling and consolidation of tailings is attributed to the presence of unrecovered bitumen, which is directly related to the efficiency of the extraction process. Additionally, the diverse electrochemical interactions between clays, water and bitumen promote the formation of more stable clay suspensions. Therefore, having knowledge of the composition and physical structure of tailings is of considerable importance to reducing the size and scale of the tailings ponds.

The slow settling of fine clay solids and the large demand for water during the oil sand extraction process have promoted research and development during the last 20 years of new technologies to reduce oil content in tailings and to improve their settling characteristics, which would also allow for enhanced water release for recycling. These advances include process modifications such as variations in pH, salinity and addition of chemical substances. Currently, the two technologies commonly used in the oil sands industry to improve tailings settling rates are the consolidated tailings (CT) process and the paste technology.

Research into oil sands mining has demonstrated that the efficiency of both the oil recovery process and the optimization of tailings settling are governed by the
petrophysical properties of the oil sands. Although plant scale improvements have been made to decrease the amount of remaining bitumen in tailings and to improve their settling rates, there is a need for an on-site fast and real time measurement of tailings composition and of their settling characteristics to identify when process modifications are needed. At present, some of the oil extraction process conditions are based on empirical correlations of decreasing bitumen content with increasing fines content (Shaw, 1996). Improved process control and efficiency requires actual measurements of tailings properties, as opposed to general correlations. Therefore, there is a requirement in the plant for making fast measurements of bitumen, water and solids content of the oil sands and the tailings, and also for real time measurements to indicate if process aids such as chemicals were successful in altering the settling properties of the tailings. Aside from reducing the environmental impact of slow settling tailings ponds, this would also lead to higher economic returns due to enhanced oil and water recovery. Thus, an improvement of the measurements of the petrophysical properties of the rock / fluid systems at various stages in the oil sands process can lead to more efficient recovery of the oil and a reduced environmental footprint from the oil sand mines.

1.2 Proposal

This study proposes the use of low field Nuclear Magnetic Resonance (NMR) technique as a non-destructive and potential on-site application in the oil sand mining process to make rapid estimations of bitumen, water and solids content in synthetic and real tailings samples. These fast measurements would also help for estimating the tailings settling rates and would directly benefit the extraction process efficiency, taking into account that the presence of unrecovered bitumen in tailings delays their settling and the recovery of this bitumen is also valuable.

Moreover, it is proposed to use the NMR technique in the study of the effectiveness of different concentrations of flocculant, coagulant or a mixture of both on the tailings
settling rates. A higher grade of effectiveness of these substances means a larger amount of water that could be reincorporated immediately into the process.

1.3 Methodology

In this study, NMR was used to characterize tailings samples under ambient conditions. The methodology applied was divided into two stages: in each stage both synthetic and real tailings samples were measured. The synthetic tailings samples were prepared to analyze the NMR responses in simple systems containing known amounts of fluids and solids. These samples were used to develop measurement protocols that yield stable spectra in reasonable measurements times (approximately 15 minutes). Once the NMR method was developed using these simple systems, real tailings samples were provided by Shell Canada and the methodology was validated against these actual tailings.

The first stage of this methodology is focused on the development of a new and fast NMR detection method to quantify bitumen, water and solids content in synthetic and real tailings samples.

The second stage of this study investigates the behaviour of the tailings settling rates in the absence and presence of different concentrations of a flocculant and / or a coagulant typically used in the oil sands process. The objective of this second stage is to identify when a tailings sample will have slow settling, which will be an indication to add chemical substances that enhance water separation. The spectra of the tailings samples after chemical addition could be then used to monitor the success of the chemical added.
1.4 Organization of the Thesis

The thesis is organized in seven chapters

Chapter 2 summarizes the fundamentals of the NMR technique and its application in oil sands extraction process.

Chapter 3 provides information about the characteristics of the oil sand deposits in Northern Alberta, a description of the bitumen extraction process used commercially by mining companies, and their tailings disposal methods. This chapter also summarizes the current treatment methods to manage fine tailings and some factors affecting their consolidation and settling.

Chapter 4 presents the methodology used in the development of a bimodal compositional detection method to characterize tailings composition.

Chapter 5 shows the results obtained from the NMR measurements of synthetic and real tailings samples, using the new method.

Chapter 6 presents the analysis of the natural settling behavior of synthetic tailings samples and the behavior of real tailings samples under the presence of different concentrations of a flocculant, a coagulant and a mixture of both substances. These are the typical chemicals used commercially to improve settling and consequently water release.

Finally, Chapter 7 provides a summary of the observations and conclusions on the characterization of the oil sands tailings using low field nuclear magnetic resonance (NMR) technique developed throughout the thesis, along with suggestions for future improvements in this area.
CHAPTER 2: FUNDAMENTALS OF THE NMR TECHNIQUE

2.1 Introduction

The NMR method for measuring nuclear magnetic moments was conceived independently in the late 1940’s by Felix Bloch and Edward Purcell. This technique is non-destructive and has been used in the petroleum industry for the past 60 years to infer both rock and fluid properties.

Fundamentally, Nuclear Magnetic Resonance (NMR) is a phenomenon that occurs when the nuclei of certain atoms are immersed in a static magnetic field and are then exposed to a second oscillating magnetic field. Some nuclei experience this phenomenon, and others do not, depending upon whether they possess a property called spin. Elements that possess a measurable spin essentially behave like tiny bar magnets, and therefore when they are placed within an external magnetic field, the movement of their nuclei can be recorded.

One of the advantages of using the NMR technique is that it is possible to monitor the interaction between porous media and the contained fluids in a non-invasive manner, which allows core samples to be re-used for multiple tests and also minimises the impact of exploration and assessment activities on the environment, through the application of NMR logging tools. Moreover, the NMR technique is relatively fast and measurements and analyses can potentially be automated in order to eliminate operator bias in the subsequent interpretation of the data. For these reasons, NMR can be considered as an alternative fast tool to provide compositional results on-site or may even be implemented on-line in a process.
2.2 NMR Physics

The fundamental bases of NMR are the absorption and emission of energy in the radio frequency range of the electromagnetic spectrum. The physics of this phenomenon is explained in detailed below.

2.2.1 Spin and the Effect of Magnetic Fields on Protons

NMR is based on the interaction between an external magnetic field and a nucleus that possesses a spin property, which is analogous to a small magnetic field surrounding the nucleus. Individual subatomic particles (protons, electron and neutrons) each possess a spin value of 1/2. Elements with even atomic weights and atomic numbers have integral values of spin. These cancel one another out, yielding a final measurable spin value of zero. A nucleus with no spin (I = 0) is NMR inactive since it will not interact with an external magnetic field. A nucleus possesses a half integral value (i.e., I = 1/2, 3/2, etc) if it has an odd atomic weight due to the presence of an unpaired proton. The nuclei used most often in NMR are those with I = 1/2 (i.e., hydrogen, phosphorus and carbon 13). The hydrogen atom is the most commonly studied nucleus in NMR because it has the largest magnetic moment; consequently it emits the strongest signal of any stable nucleus (Bervilleau, 1996). In this manner, electronic tools can be tuned to capture only the strong signal from hydrogen protons, giving rise to hydrogen NMR technology. All NMR applications in the petroleum industry are hydrogen-based measurements.

The magnetic moments of nuclei or protons orient themselves randomly in the absence of an external magnetic field. In this case, the net magnetization vector (M) is equal to zero. Protons can be thought of as spinning, tiny bar magnets with a north and a south pole, which are randomly aligned in space. However, when the protons are placed in the presence of a static magnetic field $B_0$, a torque is exerted on the magnetic moments. In the presence of this field, the protons will align or orient themselves in the direction of $B_0$ and the magnetic moments will precess with a frequency about the direction of the $B_0$. 


This frequency is known as the Larmor frequency, defined in equation 2.1. The randomization and alignment of the protons is illustrated in figure 2.1.

\[ f = \frac{\gamma B_0}{2\pi} \]  

(2.1)

Where \( f \) is the Larmor or resonance frequency (1/s) and \( \gamma \) is the gyromagnetic ratio (1 / (T · s)). Every element is characterized by a unique value of \( \gamma \). The gyromagnetic ratio for hydrogen is 267.54 MHz / T (Coates et al., 1999). Since the value of the Larmor frequency is fixed for any given element, NMR electronics can be tuned to capture the response for that element specifically.

Based on quantum theory, the magnetic moments will adopt only specific orientations. The total number of orientation states that any nuclei have is defined as \( 2(I + 1/2) \). For a hydrogen nucleus with \( I = 1/2 \), there exist two orientation states: parallel and anti-parallel to the external magnetic field lines. Protons will be at their lowest energy state when alignment is parallel to \( B_0 \), which is the preferred state. Conversely, if the protons are aligned anti-parallel, the energy state is high, so most of the protons will precess in the direction of \( B_0 \) (Hornak, 2008).

**Figure 2.1 Proton Alignments in the Absence and Presence of an External Magnetic Field (Belliveau, 1996)**
The difference between the number of protons in the parallel and anti-parallel alignment to $B_0$ will define the net magnetization term ($M$) that is measured by NMR tools. When $M$ and $B_0$ are placed on a Cartesian coordinate system, the precession of $M$ occurs around the z-axis, as presented in figure 2.2. The magnetization vector can be broken down to $M_x$, $M_y$, and $M_z$. The forces that are perpendicular to $B_0$ will cancel each other out, resulting in no magnetization on the transverse plane (x-y axes). The bulk magnetization ($M_0$) is the resultant $M_z$ (Todoruk, 2003; Hornak, 2008).

**Figure 2.2 Magnetization Vector on Cartesian Coordinates**

![Magnetization Vector on Cartesian Coordinates](image)

### 2.2.2 Longitudinal and Transverse Relaxation Times

In an NMR measurement, the protons are initially aligned with the static magnetic field, as shown in figure 2.2. A radio-frequency pulse is then applied to tip the net magnetization vector $M_0$ onto the transverse (x-y) plane. Eventually, as the protons lose the energy absorbed from the radio-frequency signal, they return back to their equilibrium direction.
Relaxation time is a time constant associated with the return of nuclear spins to their equilibrium positions after excitation. The most frequently measured relaxation times are the longitudinal relaxation time ($T_1$) and the transverse relaxation time ($T_2$).

The longitudinal, or spin-lattice, relaxation time ($T_1$) is the time constant that characterizes the alignment of spins with the external magnetic field. This is the measure of rate at which the net magnetization vector returns to the z-axis. The transverse, or spin-spin, relaxation time ($T_2$) is the time characterizing the loss of phase coherence that occurs among spins oriented on the transverse (perpendicular) plane to the main magnetic field. Transverse relaxation is due to interactions between spins, and can never exceed the longitudinal relaxation time (Coates et al., 1999).

The process for a $T_1$ measurement begins with the protons sitting in the static $B_0$. The magnetization vector aligns with $B_0$, and the vector along this axis is subsequently reduced to zero after the application of a 90° pulse to flip the protons onto the transverse plane. The time constant $T_1$ refers to the time required for the signal to grow to 67% of its final value in the direction of the z-axis. For an exponentially growing signal, this is the value used to characterize the rate that the signal increases (Farrar and Becker, 1971; Hornak, 2008).

In the case of the transverse relaxation time ($T_2$) two spin-echo sequences have been developed known as Hahn’s spin-echo method and Carr-Purcell-Meiboom-Gill (CPMG) method. The CPMG pulse sequence is preferred over Hahn’s method because it accounts for diffusional effects for an atom within a liquid, in that the spin of the atom undergoes diffusive motion as it moves from its initial position (Dunn et al., 2002; Xu and Davis, 1999). The key difference between $T_1$ and $T_2$ measurements is that in $T_2$ measurements, the signal amplitude is recorded as it decays on the transverse (x-y) plane. The $T_2$ time constant is the time required for the amplitude to decay to 33% of its original value on the transverse plane, and is the value used to characterize an exponentially decaying signal. Recalling that protons are constantly precessing due to the presence of their magnetic moments, the decaying signal on the transverse plane could be due to multiple factors.
The protons could be emitting energy and returning to their equilibrium direction, or alternatively it could be simply loss of phase coherence as a result of the protons precessing at slightly different rates. The CPMG pulse sequence was developed in order to account for the loss of phase coherence, thus the recorded decaying signal on the transverse plane will be the response only from the protons returning to the $z$-axis direction.

The CPMG sequence starts with a 90° pulse to tip the magnetization vector onto the transverse plane, followed by a series of 180° pulses. These 180° pulses re-align the precessing protons, and allow for phase-corrected measurements of the decaying signal to be obtained. The first two pulses are separated by a time period of $\tau$, whereas the remaining 180° pulses are spaced $2\tau$ apart. Echoes occur halfway between 180° pulses at times $2\tau$, $4\tau$, ..., where $2\tau$ equals the time echo or echo spacing. Measurements of the decaying signal are collected at these echo times. On multiple repetitions of the 180° pulses, the height of the multiple echoes decreases successively as a consequence of spin-spin ($T_2$) dephasing (Belliveau, 1996). As a result, the real exponential decay of the transverse magnetization is obtained. As previously mentioned, this pulse sequence compensates for the effects of magnetic field inhomogeneity, and reduces the accumulation of the effects of imperfections in the 180° pulses as well (Coates et al., 1999). The CPMG pulse sequence is shown in figure 2.3.
2.3 NMR Parameters

The parameters of the CPMG pulse sequence are defined as the echo time (TE) or the echo spacing, the number of B pulses (180° pulses), the wait-time between successive trains, and the number of trains. These parameters are generally determined according to the characteristics of the substances analyzed.

The echo time is defined as the time between 180° pulses in a CPMG sequence. This time depends mainly on the fluid type. A fluid that relaxes quickly requires a short TE in order for the signal to be refocused and measured before all its energy is emitted. The relaxation time typical of each substance also influences the determination of the number of B pulses required, since these are the number of echoes read by the NMR tool as the transverse magnetization relaxes. This means that the product of the echo time and the B pulses establishes the length of a single decay measurement; the echo time and the B pulses together determine how much of the relaxation curve is measured.

The goal in any measurement is to maximize the number of data points collected during the decay of the signal. Therefore, fast relaxing signals should be acquired at short echo times and a relatively smaller number of echoes, while slow relaxing signals require a
higher number of B pulses or echoes, but can be measured with longer echo times. The product of the echo time and the number of B pulses cannot be too small, because that would mean the transverse relaxation curve is then not completely measured. On the other hand, if these parameters are too large, the relaxation curve is not very well defined since there are not enough echoes produced to obtain accurate information of the shape of the decaying signal (Coates et al., 1999).

The wait time or polarization time defines the time between the last CPMG 180° pulse and the first CPMG pulse of the next measured decay curve at the same frequency. This parameter therefore represents the time between the end of one experiment and the beginning of the next one. The determination of this parameter must ensure that the protons are not exposed to another sequence of pulses if they have not yet aligned completely with the net applied magnetic field (B₀). If this happens, a lower amplitude value is obtained in the next experiment since not all the protons are excited to the same extent (Coates et al., 1999). The length of the wait time is related to the relaxation time of the fluid; slow relaxing fluids require longer polarization times to fully re-align with the z-axis.

Finally, the number of trains is equal to the number of times that the decay curve is measured in a single experiment; therefore, the higher the number of trains, the longer the experiment. The advantage of using a higher number of trains is that the accuracy of the result is improved since the final decay data that is output will be the statistical average of all of the individual decay measurements. The disadvantage is that the time requirement for the NMR technique is increased, and if measurement times become prohibitively long then the NMR can no longer be used as a tool for collecting data quickly, as in online measurement systems. The determination of the number of trains required depends also on the type of fluid analyzed. For instance, crude oil, with many different relaxing hydrocarbon species, requires a higher number of trains than single component relaxing species such as water or kerosene (Coates et al., 1999).
2.4 Relaxation Mechanisms in Fluids

Fluids in porous media that are exposed to magnetic field gradients can relax through three processes: bulk, surface and diffusion relaxation (Kleinberg et al., 1994; Kleinberg and Vinegar, 1996; Straley et al., 1997; Slijkerman and Hofman, 1998).

2.4.1 Bulk Relaxation

Bulk relaxation is a property of the fluid, and is caused by local diffusion of the fluid molecules. Basically, this is the relaxation if the fluid were put in a large container within a homogeneous magnetic field. The bulk relaxation rate of a fluid is proportional to fluid viscosity (Straley et al., 1997). Based on this relationship, it is evident that a low viscosity fluid like water will have a slow bulk relaxation rate, with a $T_2$ relaxation time on the order of two seconds (Coates et al., 1999). In the case of conventional oils, whose viscosity is slightly higher than water, the $T_2$ values will vary from similar $T_2$ values for water, down to a few hundred milliseconds. Heavy oils and bitumen, which are more viscous than either water or conventional oil, will have $T_2$ values less than 10 ms. Therefore, the $T_2$ values measured by bulk relaxation of fluid are directly correlated to the fluid viscosity (Kleinberg, et al., 1996).

During the relaxation process of any substance, energy must be exchanged between spins of different protons and the rate at which this happens is limited by molecular motion (Brown et al., 1960). Consequently, low viscosity fluids have high molecular mobility, which leads to slow relaxation rates and high values of relaxation times. Oppositely, high viscosity fluids have a reduced molecular mobility, which increases the relaxation rates and reduces the subsequent relaxation times.
2.4.2 Surface Relaxation

Surface relaxation in fluids occurs when energized protons in one fluid approach the interface of another fluid, or the interface between the fluid and a solid. Since the properties of the fluid and solid are different, an opportunity exists for energy to be lost from the fluid, through contact with the walls or the interface with the other fluid (Kenyon, 1997). Surface relaxation rate is described by equation 2.2 (Straley et al., 1997).

\[
\frac{1}{T_{2s}} = \rho S \frac{V}{V}
\]  

(2.2)

Where \(T_{2s}\) is the decay time for the fluid on the surface of the porous media, \(\rho\) is the surface relaxivity and \(S/V\) is the surface area to volume ratio of the pore or droplet containing the fluid.

Surface relaxivity (\(\rho\)) provides a measure of the probability of energy being lost through collisions. According to equation 2.2 (\(\rho\)) is a proportionality constant between the \(T_{2s}\) decay time and pore size (Slijkerman and Hofman, 1998). A high value of surface relaxivity for a given porous medium implies that a proton colliding with a rock surface will emit a lot of energy and relax substantially with each collision. In the case of water constrained in a water-wet rock, this type of relaxation is dominant because water contacts the pore walls quickly (Coates et al., 1999). For a low viscosity fluid such as water relaxing in a porous medium, the surface relaxation rate is significantly faster than the bulk relaxation rate. Therefore, the measured relaxation (the sum of bulk and surface relaxation) is essentially equal to the surface relaxation rate. Since surface relaxation is itself directly proportional to \(S/V\) of the porous medium, it is commonly accepted that NMR spectra of water in porous media are essentially analogous to a measurement of the pore size distribution of the rock (Straley et al., 1997).
2.4.3 Diffusion Relaxation

The original magnetic field $B_0$ is generally not homogeneous, which leads to the generation of magnetic fields gradients. The presence of these gradients means that not all the protons have the same energy as they precess on the transverse plane, since they were not all exposed to the same value of $B_0$. As a result, they will not emit the same energy in each pulse of the CPMG sequence, and this leads to additional de-phasing of the protons during the measurement. Since molecular motion is random, the dephasing is irreversible and relaxation appears to happen faster than it would have in the absence of these field gradients. The rate of diffusion relaxation can be calculated using the equation 2.3 (Kenyon, 1997).

\[
\frac{1}{T_{2D}} = \frac{D(\gamma GTE)^2}{12}
\]  \hspace{1cm} (2.3)

Where $1/T_{2D}$ is the transverse relaxation caused by diffusion of molecules in a field gradient, $D$ is the self-diffusivity of the molecules, TE is echo time and $G$ is the magnetic field gradient.

If a fluid with a significant value of $D$ is analyzed, the relaxation due to diffusion in field gradients can mask the other relaxation processes. While this has applications in NMR measurements in gas reservoirs, most laboratory research using the NMR technique attempt to reduce this parameter as much as possible (Straley et al., 1997). NMR tools have windows of relatively constant magnetic strength, where $G$ is approximately zero. Moreover, the magnitude of $G$ is proportional to the field strength, which is small in low field NMR. The effects of diffusion are generally only noticeable for gas, where $D$ value is large (Kleinberg et al., 1996), but are negligible in measurements of viscous oil and water. In the absence of enhanced relaxation due to diffusion through magnetic field magnetic gradients, there is no longer additional $T_2$ relaxation, so $T_1$ and $T_2$ are essentially the inverse of one another.
2.5 Processing of NMR Data

The total measured NMR signal is the sum of the effects from different fluid components (bulk relaxation effects) and the effects of the fluids distributions (surface and diffusion relaxation). In porous media, each fluid relaxes at a rate that is the sum of its bulk and surface relaxation. For most systems, therefore, the final decay curve cannot be fitted as a single exponentially decaying compound. The measured signal is instead fitted to a multi-exponential decay curve as shown in equation 2.4 (Coates et al., 1999):

\[ A_T = \sum A_i \exp(-t/T_{2i}) \]  

(2.4)

Where \( A_T \) is the total NMR signal on the transverse plane, \( A_i \) is the amplitude corresponding to a single relaxation component, \( t \) is time and \( T_{2i} \) is the time constant associated with the amplitude \( A_i \).

In order to separate the effects of the different relaxation mechanisms, the raw spin-echo data obtained from NMR needs to be processed to obtain a distribution or spectrum of amplitude against relaxation times (\( T_2 \)). In practice, this is done through a non-negative least squares regression (NNLS), whereby the measured decay curve is fit into a set of pre-defined \( T_2 \) bins. The associated \( A_i \) values are found such that the errors are minimized between the actual and re-processed decay curve. In this work, all the NMR relaxation data was processed using ExpFit\textsuperscript{®}, which is internal software that was developed in TIPM Laboratory. This program performs the NNLS regression, which can be found in the open-source literature. The data are fit into 51 pre-defined \( T_2 \) values, equally spaced on a logarithmic time scale between 0.1 to 10,000 ms.

The output from the inversion software is the distribution of amplitudes that best fits the set of chosen \( T_2 \) terms. This is known as an NMR spectrum, and the information observed in NMR spectra allows for a determination of fluid properties, solids properties and fluid mobility.
Figure 2.4 shows an example of a NMR spectrum of a mixture of solids and water. In this spectrum, the peaks relaxing at around 10 ms corresponding to the water bound to clays, since this signal is significantly faster than the bulk water peak that is relaxing after 1000 ms. Since the mixture only contained the signal from a single low viscosity fluid (water), the peaks at early relaxation times must come from water that is in a physically confined location. In bulk water, the S/V is essentially zero since there is a negligible surface area of an interface, so the water is relaxing through bulk relaxation. As expected through theory, the NMR spectrum can therefore be used to interpret the fraction of water that is free compared to the water that is relaxing in the solids.

Conversely, figure 2.5 presents the NMR spectrum of 1.5 g of Cold Lake bitumen, which has a viscosity of approximately 70,000 mPa·s at room temperature. Although this oil is a bulk fluid (i.e. there is no surface relaxation effect) the fluid still exhibits a fast relaxation time of less than 1 ms. This is because the protons in the oil are restricted due to its high viscosity, so the bulk relaxation rate is very fast. The consequence of this is that for viscous fluids, bulk relaxation may mask any effect of surface relaxation so information regarding the physical location of the fluid may be lost.

Figure 2.4 NMR Spectra of a Mixture of Solids and Water
2.6 Other Important Relationships

Parameters as the fluid amplitude index (AI), geometric mean relaxation time ($T_{2gm}$) and signal to noise ratio (SNR) are other parameters used during this study to gather information about mass predictions; settling characteristics and the presence of noise in the signals obtained from the NMR tool.

2.6.1 Amplitude Index (AI)

The signal of a given fluid is directly proportional to the measurable amount of hydrogen present in the fluid. This is quantified by the fluid’s hydrogen index, which is defined as the moles of hydrogen per unit volume of test liquid, referenced to the moles of hydrogen per unit volume of water (Kleinberg and Vinegar, 1996). Moles of hydrogen are not easy to measure directly, so in practice the measured amplitude is simply related to the amount (mass or volume) of fluid present. In experiments performed at the Tomographic Imaging in Porous Media (TIPM) Laboratory (Mirotchnik et al., 2001), it was observed that the relationship between the cumulative amplitude of a given fluid (oil or water) and the mass of the fluid is linear. This relation is presented in equation 2.5:
\[ m_{\text{fluid}} = \frac{A_i}{A} \]

(2.5)

Where \( m_{\text{fluid}} \) is the mass of a given fluid within the sample (g), \( A_i \) is the cumulative total amplitude of the spectra and \( A \) is the amplitude index of the single fluid. Therefore, if the amplitude index of oil or water is known, then the mass of the fluid in an unknown sample can be calculated using this equation.

Specifically, the AI of a fluid is found by measuring different amounts of the same substance, and correlating their masses with the amplitude values. The amplitude index is the slope of the line relating the amplitude to the fluid mass.

2.6.2 Geometric Mean of Relaxation Time (\( T_{2gm} \))

The mean of the \( T_2 \) distribution is called the geometric mean relaxation time, or the weighted average of \( T_2 \). The mean is a logarithmic average, since the \( T_2 \) values in an NMR spectrum are plotted on a logarithmic scale. For a single exponentially decaying fluid such as water, the relaxation time of the fluid can be expressed as essentially a single value of \( T_2 \). For more complex systems such as oil or water in multiple pore sizes, the fluid relaxation time is better described by this mean value. In this manner, \( T_{2gm} \) is used to characterize the overall property of \( T_2 \) and is calculated using the equation 2.6 (Straley et al., 1997):

\[
\ln T_{2gm} = \frac{\sum_i A_i \ln(T_{2i})}{\sum_i A_i} \\
T_{2gm} = \exp\left(\sum_i \frac{A_i \ln(T_{2i})}{A_i}\right) \\
\]

(2.6)

Where \( A_i \) is the amplitude value corresponding to a specific relaxation time \( T_{2i} \) (s) and \( A \) is the cumulative total of the signal amplitude. For fluids relaxing in confined spaces, \( T_{2gm} \) shown in the equation 2.3 determines the degree of peak shift in the spectrum,
compared to the bulk relaxation time of the fluid. This is very useful in settling analyses, since this value is related to the average pore size of the porous medium constricting the water relaxation. Furthermore, it has been found that when measuring the invasion of water into porous media, the $T_{2gm}$ value can be used to interpret the wettability of the medium (Manalo, 2001; Hum and Kantzas, 2006).

### 2.6.3 Signal to Noise Ratio (SNR)

Signal to noise ratio is the ratio of signal amplitude compared to the noise amplitude, and is utilized as an indication of the quality of the measured data. The signal refers to the desired part of a detected measurement, and is due to the amplitude of protons present in the magnetic field. Noise refers to the remainder of the detected signal and includes random noise or systematic electronic oscillations (Coates et al., 1999).

The SNR value obtained in each measurement can be used as an indication of how well an NMR tool is functioning. If this value is high, this means that the signal obtained comes principally from the substance analyzed; whereas a low SNR value indicates that a high presence of noise is present from the environment or the electronics of the apparatus.

Generally, the effect of noise is especially prominent at early relaxation times; therefore when noise is present this can be wrongly assumed as signal coming from the substance being analyzed. This factor must be taken into account when performing measurements on substances with early relaxation times, such as high viscous oils.

### 2.7 Previous Work in Oil Sands Using NMR Technique

Previous experience has shown that low field Nuclear Magnetic Resonance (NMR) has considerable potential for the characterization of cores containing conventional oil, water and gas. In recent years, significant progress has also been made in NMR applications for heavy oil reservoir characterization.
In these reservoirs, one of the most significant parameters to be determined is the oil viscosity. Measurements of heavy oil and bitumen from multiple formations, and at multiple temperatures, led to the identification of a new NMR viscosity model (Bryan et al., 2003; 2005a). It was observed that, as expected, oil $T_{2gm}$ values would decrease with increasing oil viscosity. However, for high viscosity bitumen the relationship between viscosity and $T_{2gm}$ becomes non-linear, and significant increases in viscosity are only accompanied by small changes in the oil relaxation times. The oil amplitude index was also observed to correlate with the oil viscosity (Galford and Marschall, 2000; Mirotchnik et al., 2001): as the oil viscosity increased, the oil amplitude index would decrease accordingly. Therefore, the improved heavy oil viscosity correlation (Bryan et al., 2003; 2005a) incorporated both of these parameters in the prediction of viscosity. Recently, attempts have been made to extend this model to in-situ viscosity predictions (Bryan et al., 2005b; 2007; Burcaw et al., 2008).

An additional topic of considerable interest in recent years has been the determination of oil and water content in fluid streams containing viscous bitumen and water. In thermal operations or heavy oil waterfloods, it is often difficult to measure the oil and water content in produced fluid streams. These measurement concerns have led to the development of NMR water cut metering tools (Allsopp et al., 2001; Wright et al., 2002; 2004; Kantzas, 2004). A key consideration in water cut measurements is that even at elevated temperatures, the viscosity difference between bulk oil and water leads to separation in their NMR signals. By summing up the oil and water amplitudes and dividing by their respective amplitude indexes, it is possible to measure the masses of oil and water in the sample.

Some progress has also been made for extending these measurements to three phase systems such as oil-water-air or oil-water-solids, where the third phase is determined by difference from the total sample mass or volume (Bryan et al., 2002; Ding et al., 2004). This is the same general procedure that is followed in tailings characterization in this
study; oil and water amplitudes are converted into their respective fluid masses, and the solids content is found by difference from the total sample mass.

The last major area of research in NMR applications in oil sands is in characterization of oil sands mining samples. The NMR technique has been used in the characterization of literally hundreds of ores and froths from northern Alberta mining operations (Kantzas et al., 2005; Bryan et al., 2006; Mai et al., 2006; Niu et al., 2008). Each test consisted of a measurement of the sample mass and its NMR spectrum. The nature of the in-situ fluid signals would then be inferred based on the properties of the NMR spectra and using calibration parameters, such as the spectra of pure fluids. The goal of all of these measurements was to use NMR as a tool for making fast predictions of oil, water and solids content in ores and froths. Due to inaccuracies identified in the separation of oil and clay bound water signals (Mai et al., 2006), subsequent analyses also included a measurement of the bulk density of the sample, which could then be used to improve the prediction of the oil content (Niu et al., 2008). In the development of this technology, NMR predictions are compared against measured oil, water and solids fractions obtained by Dean Stark extraction, which is the standard technique accepted by the industry. The eventual goal of this work is to generate confidence in the NMR measurements, such that the Dean Stark procedure can be replaced. This will save significant time and money for operators of oil sands mining and extraction operations.

In the interpretation of NMR spectra of oil sands, another important parameter for characterizing the samples is the grade of the ore (i.e., the ease with which oil can be separated from the solids). This is directly related to the fines content. In several studies synthetic samples with different clays (illite, kaolinite and sodium montmorillonite), sand, and brine were created to simulate ores of varying recovery grades (Manalo and Kantzas, 2003; Hum and Kantzas, 2005; 2007; Chung and Kantzas, 2007). In some of those samples, bitumen was also added in various amounts to investigate the separation of oil and water when significant clay fractions were present. The results from these samples show the potential errors that can occur in determining oil content in samples
with high fines, since the relaxation times of the clay bound water are in the same $T_2$ range as the bitumen.

The other significant finding from measurements of synthetic samples containing clay and water is that the clay content can potentially be determined based on the $T_{2gm}$ values of the water. For mixtures containing illite, kaolinite, montmorillonite, sand and brine, it was shown that clay bound water has a characteristic response. These NMR 'signatures' could therefore be used to develop predictive nomographs of clay content (Hum and Kantzas, 2007). The signal from the clay is highly dependent on the clay type and also on the salinity of the brine (Chung and Kantzas, 2007; Chung, 2007). In order to properly characterize the response in clay-water systems, it is very important to have some knowledge of which clays are present, and the influence of the brine salinity on the final water $T_{2gm}$ values.

The previous work in oil sands mining samples has focused mainly on settled solids, where water is located in the pores of the sand and clay. When solids are suspended, as is the case for tailings, it is not clear how these correlations and nomographs can be used to predict the clay content. Moreover, the previous samples with oil all contained relatively high oil content, so the predictive nature of NMR for low oil content like those found in tailings has not been addressed. Tailings are unique in their makeup and characteristics, so these differences will be the main focus of the research in this thesis.
CHAPTER 3: OIL SANDS AND TAILINGS PROPERTIES

3.1 Introduction

Oil sands are unconsolidated sand deposits composed of sand, clay, water, and high molar mass viscous petroleum, which is denominated bitumen. The major accumulations of oil sands are distributed in eight countries: Canada, Venezuela, USA, Trinidad, Madagascar, Albania, Russia and Romania, with Canada and Venezuela being the two largest sources of bitumen in the world. Over 95% of the known in-place oil volumes are located in Canada, specifically in three areas up in Northern Alberta: Athabasca, Peace River and Cold Lake (Chalaturnyk et al., 2002). The Athabasca deposit is the largest of the Canadian oil sand deposits and is the only one shallow enough to be partially amenable to mining techniques (Carrigy, 1973). The bitumen deposits in Northern Alberta cover six million hectares of sedimentary formations of sand and carbonate (NEB-EMA, 2004). Figure 3.1 shows the location of the three main oil sands deposits.

Figure 3.1 Alberta’s Three Oil Sands Areas (Modified by AEUB, 2007)
Oil can be recovered from the oil sands deposits through surface mining and in-situ recovery techniques. Surface mining is economically feasible when the oil sand reserve is at depth of less than 75 m, and it is estimated that about 15-20% of the reserves are at this depth. The remaining 80-85% is recovered through in-situ recovery techniques such as SAGD or VAPEX because the oil with zero mobility is buried at depths that are too great for surface mining to be performed (Butler and Yee, 2002). In commercial production systems, bitumen comes from deposits buried less than about 50 metres for surface mining and more than 400 metres for in-situ recovery. After mining the oil sand, the bitumen is extracted from the sand by a hot water flotation process known as the Clark Hot Water Extraction Process (CHWP), which was developed by Dr. Karl Clark in the 1920’s (Shaw, 1996). Subsequently, the extracted bitumen is upgraded by refinery processes to produce synthetic crude oil (SCO).

The first commercial surface mining plant to recover bitumen from oil sands was initiated by Suncor Inc. in 1967, followed by Syncrude Canada Ltd. in 1979 and subsequently by Albian Sands Energy Inc. in 2003. In recent years, some other oil companies such as Canadian Natural, Imperial Oil, Total, Petro-Canada, among others, have also begun the process of developing mining operations in Northern Alberta.

Based on the current available data, the Alberta Energy and Utilities Board (AEUB) estimates that the ultimate oil-volume-in-place is 2.5 trillion barrels (AEUB, 2005). Of this amount, 140 billion barrels are recoverable through surface mining and the remaining 2.4 trillion barrels are amenable to in-situ recovery. According to the Canadian Association of Petroleum Producers (CAPP), in 2005, the oil production from Canada oil sands reserves was close to 1.3 million barrel per day, and it is expected that the total bitumen production will reach 1.8 million barrels per day by 2020 (CAPP-Canadian Crude Oil, 2006). In 2006, oil sands mining operations accounted for almost 60% of all oil sands production (CAPP- Reserves at December 31, 2006). The recovery factors from these operations are considerably higher than in-situ bitumen recovery: Syncrude and Suncor report bitumen recovery efficiencies of 92 and 90% for ores containing 12 wt %
bitumen (Chalaturnyk et al., 2002). These high potential recoveries, coupled with the significant mineable oil reserve base, makes mining operations very attractive for oil sand recovery.

During oil extraction from the oil sands mines large volumes of solid and liquid materials are generated and must be reclaimed. For each barrel of synthetic crude oil produced, about 2 tonnes of oil sands are processed, with a by-product of 2 m$^3$ of processed water and 1.8 tonnes of solid tailings. The tailings stream is a mixture composed primarily of water, sand, silt, clays and a small amount of unrecovered bitumen. Conventionally, tailings are discharged of into ponds where the segregation between coarse sand and fine clay solids occurs. In these tailings ponds, coarse sand settles rapidly while fine clay solids settle slowly. As a result, disposal of these fine tailings is a serious environmental problem because natural full consolidation of the fine solids is estimated to take thousands of years. Aside from the obvious reclamation issues associated with such slow settling, this is also an unfavourable factor in the recirculation of water into the production process. The accumulated volume of mature fine tailings is expected to increase to over one billion cubic meters by the year 2020 (Masliyah, 2007). In recent years, significant efforts have been spent characterizing these tailings, and developing ways to more efficiently handle tailings disposal.

### 3.2 Oil Sands Characteristics

Athabasca oil sands contains bitumen from 0 to 16 wt % and averaging 12 wt %, water content between 3-6 wt %, increasing as bitumen content decreases, and mineral content (quartz, silts and clays) from 84 to 86 wt % (Masliyah, 2007). Clays are present in the form of discontinuous bands varying from 1 to 15 cm in thickness. The oil saturation has shown to be affected by the high water absorption capacity of clays, which reduce the permeability to oil; consequently, oils sands with high clay content generally correspond to lower oil content zones (Carrigy, 1962).
Oil sands saturations are classified as rich (12-14 wt %), average (10-11 wt %) and lean grade (6-9 wt %). Lower than 6 wt % bitumen is not considered to be of “ore-grade” quality, and will likely not be economic to mine. Although the bitumen content varies for different zones, the total content of formation water and bitumen is generally approximately 16 wt % with the remaining 84 wt % is constituted of mineral solids (Masliyah, 2007).

In general, the oil sands have higher porosities (25-35 %) than most petroleum reservoirs (5-20 %) (O’Donnell, 1984). This high porosity is attributed to the low occurrence of mineral cements (Mossop, 1980). The ranges of porosity and permeability found in the Athabasca area are 30-35 % and up to 5000 md (milidarcy), respectively. Conversely, the permeability of undisturbed oil sand can be as low as about 50 md or less, but for oil that has been mined is in the order of several Darcys (Clark, 1960).

3.2.1 Oil Sands Structure

The Athabasca oil sands are composed mainly of quartz sands grains, which are hydrophilic and 99 % water wet (Bowman, 1967). If this is true, it means that the bitumen is not in direct contact with the mineral phase because a thin film of water surrounds individual sands grains. The thickness of the water film is predicted to be about 10 nm (Takamura, 1982; Hall et al., 1983). This water film is assumed to be stabilized by electrostatic forces coming from electrical double layers at the oil/water and water/sand grain interfaces (Takamura, 1982; Hall et al., 1983; Anderson, 1986). Alternatively, the porous medium may consist of fine clay particles surrounded by aqueous films; evidence has shown that a substantial amount of fines are present in the form of thin discontinuous beds (Cottrel, 1963; Cameron Engineers, 1978; Takamura, 1982). The usual representation of oil sand structure proposed by Takamura in 1982 is shown in figure 3.2.
3.2.2 Bitumen Characteristics

Bitumen is chemically similar to conventional crude oil but it has a greater density and a much higher viscosity.

Bitumen density is higher than that of heavy oil, and is very close to water. This is an important factor in the bitumen flotation process since this requires a density difference in order for oil to move to the top of the separation vessels. Therefore, air is also required as an additive to effectively reduce the density of the oil and cause the oil droplets to rise during frothing.

Bitumen viscosity in-situ varies from several hundred to several tens of thousand Pascal-seconds (Carrigy 1967). The viscosity of Athabasca bitumen is about 1,000,000 mPa·s at reservoir temperature, making the bitumen practically immobile; however, this characteristic gives enough material strength to the oil sands to be mineable (Mossop, 1980; Farouq Ali, 1974). The bitumen viscosity is approximately one order of magnitude higher than Cold Lake heavy oil (Masliyah, 2007).
3.2.3 Mineral Solids Characteristics

The mineral composition of the oil sands is over 90% quartz with small amounts of muscovite, feldspar and chert (Carrigy and Kramers, 1973; Boon, 1978). The typical clays found in the oil sands are kaolinite (40-70 wt %), illite (28-45 wt %) and a small proportion of montmorillonite (1-15 wt %). Structurally, kaolinite does not have a high affinity to water and thus will exhibit little swelling characteristics. Illite also has a very poor structural affinity to water and its swelling characteristics are not good. Conversely, montmorillonite has the highest affinity to water and swells when hydrated (Rogers, 1953). Kaolinite has the highest anion exchange capacity, followed by illite and montmorillonite, in that order. This means that, aside from issues of clay swelling for different clay types, the clays may also interact with the salts or surfactants generated in the extraction process. These characteristics of the clays are important for the formation of a gel-like structure in tailings management options and for the ion exchange mechanism in the tailings ponds (Chalaturnyk et al., 2002).

Clay minerals only appear in the fines fraction. The terminology adopted in the industry for “fines” is that portion of mineral that is smaller than 44 microns and is further subdivided into silt-sized (< 44μm > 2μm) and clay-sized (< 2μm) particles (Kingsley, 1996). The mineral solids particle size distribution (PSD) is a very important factor for bitumen flotation during the hot water extraction process and for the design and operation of tailings and hydrotransport pipelines. Small fractions of heavy minerals may also be found in the minerals of the oil sands, mainly titanium dioxide (TiO₂) and zirconium dioxide (ZrO₂), in average proportions of 0.35 % and 0.032 % respectively (Liu, 2006).

3.2.4 Connate Water Characteristics

The connate water of the oil sands contains concentrations of sodium and chloride ions from 10-1000 mg/kg of oil sand. Calcium and magnesium can vary up to about 40 mg/kg
of the oil sands. Inorganic ions such as potassium (K⁺) are also present in the formation water. Generally, for higher concentrations of ions in the water, the bitumen content will be lower; this means that rich oil sands have a low salt content and poor oil sands have a high salt content. The pH of most of the oil sands is between 8 and 9, with some acidic ores at higher depths (Masliyah, 2007).

3.3 Bitumen Extraction from Oil Sands Process

The bitumen recovery process currently used by Suncor, Syncrude and Albian Sands Energy Inc. is fundamentally the same, and is composed of seven stages. Some variations in the three processes are found mainly in the tailings and middlings treatment, and in the type of solvent used in the froth treatment.

A schematic of the Muskeg River Mine Extraction Pilot Plant employed by Albian Sands Inc. and a simplified block diagram of elementary process steps of the hot water flotation process for Athabasca oil sands are shown in figures 3.3 and 3.4, respectively. Each one of the stages involved in the bitumen extraction process is explained as follows.

3.3.1 Mining of Oil Sands

The first stage in the bitumen extraction from the oil sands deposits is to remove approximately 30 m of overburden material prior the oil sand ore can be mined. The ore body thickness generally varies from 20 to 90 m (Shaw et al., 1996). Currently, the mining of the oil sands is performed by a shovel/truck/hydrotransport system that is more energy efficient than the dragline/bucketwheel/conveyor system used in the past.

3.3.2. Oil Sands Conditioning

The oil sand is conditioned by slurrying with recycle process water in cyclo-feeders or rotational horizontal drums, called tumblers, for about five minutes (Shaw et al., 1996). Hot water, steam and caustic soda (NaOH) are then added to the oil sands in the tumblers
where heat and agitation are used to overcome the forces that hold oil sands lumps together. The mass ratio of oil sand: water: NaOH is generally of 1: 0.3: 0.00025 and the oil sand is conditioned at 80-85°C and a pH of 8.0-8.5. The slurry temperature discharge is between 70-80°C (Masliyah, 2007). During this ablation process, the layers of each lump are warmed and sheared off until everything is dispersed.

The addition of the hot water and caustic soda are the fundamentals of the Clark Hot Water Extraction Process (CHWP). The amount of added soda at the inlet of the tumbler is adjusted to raise the solution pH and to maximize bitumen recovery. The main role of the caustic soda is to produce natural surfactants from bitumen by means of the solubilization of their asphaltic acids in water. These acids are partly aromatic and contain oxygen functional groups such as phenolic, carboxylic and sulphonic compounds. Under optimal alkaline conditions, sufficient acids are released and converted into their surface-active form. In this manner the elevated pH levels are simply a reflection of the condition whereby the acids have been released; the improved separation of oil from solids is due to the presence of these surface-active acids, not the pH alone. The solubilization of the acids into water produces a reduction in the surface and interfacial tensions of the suspension; consequently, the oil sands ore structure is disintegrated and the bitumen can be recovered (Baptista and Bowman, 1969; Moschopedis et al., 1977).

The mixture of soda with hot water provides the most optimal conditions for repelling bitumen from the water film surrounding the sand, which essentially acts like a detergent and eventually disintegrates the oil sand structure. The application of heat, shear and the formation of surfactants all work to cause the sand to effectively become more water wet, and separate the bitumen from the sand grains. Good processing ores contain more natural surfactants in the oil, thus they require less amounts of soda to facilitate the initial conditioning.
3.3.3 Digestion of Oil Sands Lumps, Bitumen Liberation and Aeration

After the ablation of the oil sands lumps, the bitumen starts separating from the sand grains forming bitumen droplets within the slurry. This next step is known as the “liberation” stage, whereby the bitumen droplets are coalesced and separated from the water. Due to similar oil and water densities, air is sparged into the system and air-attachment is the other phenomenon that occurs either during the tumbler oil sand feed or the slurry agitation. The purpose of the air attachment is to effectively reduce the density of the bitumen phase by causing the oil to spread over the bubbles of gas, which allows for future gravity separation of the phases.

The slurry is discharged from the tumblers to vibrating screens and washed with hot spray water to remove over solids and undigested oil sand lumps. The rejected solids (about 5% of the original oil sand) are transported out of the plant for disposal (Shaw et al., 1996).

3.3.4 Separation of the Aerated Bitumen Aggregates from the Water-Solids Slurry

The discharged slurry coming from a tumbler or a hydrotransport pipeline contains about 7% aerated bitumen droplets, 43% water and 50% suspended solids. This slurry is diluted with water to a density of about 1450 kg/m³ and then fed to large gravity separation vessels known as primary separation vessels (PSV) or primary separation cells (PSC). These vessels are maintained in a quiescent condition to facilitate oil flotation, as well as to the settle coarse solids to the bottom. The density of the aerated bitumen droplets and mineral solids is about 500 – 700 kg/m³ and 2650 kg/m³ correspondingly. The residence time of the slurry in a separation vessel, in the case of Syncrude’s process, is about 45 minutes (Shaw et al., 1996). The residence time is an important process parameter in the optimized recovery of oil; poorer quality ores will not separate phases as easily, and may require additional time for the high oil content froth to rise to the top of the vessel.
The coarse solids settle rapidly in the bottom of the vessel and they are withdrawn as a concentrated suspension denominated primary tailings. The smaller suspended solids that do not settle quickly and the poorly aerated bitumen droplets that do not float rapidly are all drawn off in a slurry from the middle of the vessel, and are called middlings. These middlings may contain significant oil and clay, thus they are sent for further processing to recover additional oil and to optimize the settling of the solid suspension.

In order to improve the flotation and sedimentation processes, the density and viscosity of the middlings region is kept low by adjusting the flood water addition and middling removal rates, since an increase in the slurry viscosity can be caused by a clays build-up (Camp, 1976). Therefore, proper process control of the middlings requires knowledge of the oil content and the clay content in the stream. The middlings and the primary tailings streams are combined and pumped to a special tailings oil recovery (TOR) flotation circuit to recover the remaining bitumen.

### 3.3.5 Bitumen Flotation

The floated bitumen is denominated as primary froth and contains on average 60 % wt bitumen, 30 wt % water and 10 wt % solids; however this composition depends on the ore quality (Schramm, 1988). The remaining un-aerated bitumen is recovered from the middlings and primary tailings using induced air flotation in flotation cells, tailings oil recovery vessels, cyclo-separators or hydrocyclones, and is called secondary froth. The primary froth has a higher quality than secondary froth; therefore, the secondary froth also needs be cleaned in stirred thickeners to remove some of the water and the solids.

### 3.3.6 Froth Treatment

The primary and secondary froths are combined into a single feed and are de-aerated in towers by allowing the aerated bitumen to cascade over a series of cones, flowing counter-currently to an upward flow of steam. This de-aerated froth contains approximately 60 wt % oil, 30 wt % water, and 10 wt % solids. This composition is
essentially the same as the primary froth because secondary froth contributes for only 5% of the total bitumen production. The de-aerated froth is then processed in a froth treatment plant to remove solids and water. The froth is first diluted with naphtha or hexane in order to reduce the bitumen viscosity and to disrupt the emulsion stability, which allows water and solids to separate the bitumen. Subsequently, the diluted froth is centrifuged in scroll type centrifuges where coarse solids are removed.

Suncor and Syncrude use naphtha as their diluent and Albian Sands Inc. uses hexane, which is a paraffinic diluent that leads to asphaltene precipitation. The use of this diluent produces clean bitumen with small amounts of solids and water since the precipitated asphaltenes act as a flocculants to the emulsified water droplets and fine solids in the diluted froth.

3.3.7 Tailings Management

Tailings streams are managed differently in the Syncrude, Suncor and Albian processes. In the Syncrude process, the tailings and middlings streams from the gravity separation vessel are combined and sent to a secondary separation vessel known as the tailings oil recovery (TOR) unit, where additional bitumen is recovered. The TOR froth is recycled to the primary separation vessel. At Suncor, the middlings stream is directly processed in conventional flotation cells, similar to the primary separation vessels. In these vessels, more air is added to facilitate improved separation between bitumen and water. The bitumen recovered from the middlings stream by the flotation cells is termed secondary froth, which is of lower quality since its high water and solids content.

At Albian, the middlings stream is introduced to the primary flotation cells to recover additional bitumen. In these flotation cells, air is injected directly into the mixture through a central shaft and further shear is applied to improve separation. The tailings stream from the primary separation vessel is combined with the tailings stream from the primary flotation cells and is introduced to the secondary flotation cells to recover any residual bitumen. At this stage, the bitumen recovery is assumed to have been optimized,
and the remaining challenge is to maximize the settling of the solids, which will limit the tailings volume and also yield more water for recycling. The tailings from these secondary flotation cells are cycloned, with the cyclone overflow (fine tailings) pumped to thickeners and the cyclone underflow (coarse tailings) pumped to tailings ponds. The fine tailings are treated with flocculants to facilitate further water recovery, and then are thickened and pumped to a tailings pond.

In summary, in the Suncor and Syncrude operation plants, the tailings from the primary and secondary flotation processes are combined with the aqueous tailings from the froth treatment process and are transported directly to tailings ponds. In contrast, the Albian process uses cyclones and a large thickener to reclaim warm water for recycling (Masliyah, 2007).

Although tailings streams are managed in a different way for these three companies, the final tailings stream is, in general, a warm aqueous suspension of sand, silt, clays, residual bitumen, salts, surfactants and naphtha or hexane at a pH between 8 and 9. This mixture is pumped to large tailings ponds where settling of coarse solids occurs faster than fine solids. This slow settling of the fine clay solids and the large demand for water during oil sand extraction processes have promoted research and development of new technologies during the last 20 years to modify the water release and to improve settling characteristics of tailings. These include process additives such as variations in pH, salinity and addition of chemical substances. Currently, the two technologies used most commonly in the oil sands industry are the consolidated tailings (CT) process and the paste technology. Gypsum is used in the CT process as a coagulant while polyelectrolytes, generally polyacrylamides of high density, are used as flocculants in the paste technology. A detailed review of the tailings characteristics and sludge problems is presented in the next section.
Figure 3.3 Muskeg River Mine Extraction Pilot Plant (Masliyah, 2007)
Figure 3.4 Simplified Block Diagram of Elementary Process Steps in the Hot Water Flotation Process for Athabasca Oil Sands (Shaw et al., 1996)

**Conditioning**
- ablation of lumps
- dispersion of solids and bitumen
- mixing of reagents
- chemical reactions
- modifications of interfaces by adsorption
- introduction and dispersion of gas

**Aggregate Formation and Destruction**
- approach of bitumen to bubbles via external forces
- approach of solids to bubbles via external forces
- approach of bitumen to solids via external forces
- approach of similar phases via external forces

**Flotation - Sedimentation**
- approach and attachment or repulsion of bitumen - bubbles via interfacial forces
- approach and attachment or repulsion of solids - bubbles via interfacial forces
- approach and attachment or repulsion of solids - bitumen via interfacial forces
- approach and attachment or repulsion of similar phases via interfacial forces

**Froth Formation**
- aggregate transport
- bitumen - gas flotation
- formation of froth
- solids sedimentation

**Product out**
3.4 Tailings Characteristics and Disposal

As mentioned previously, oil sand tailings are produced as a by-product of the bitumen extraction process and are deposited in large tailings ponds. In general, tailings are characterized by having poor consolidation and water release properties. The tailings slurry is a mixture of sand particles, dispersed fines, water and residual bitumen. It contains approximately 55 wt % solids, of which 82 wt % is sand, 17 wt % are fines smaller than 44 μm and 1 wt % is residual bitumen. When tailings are pumped into the tailing ponds, the coarse solids settle out very rapidly to form dykes and beaches. Most of the fines and residual bitumen are carried in the run-off slurry that flows over the already formed beach. The run-off slurry stream arrives at the water’s edge in the tailings pond with a suspended solids concentration of about 3-8 wt %. These fine tailings solids settle quickly over several days to create a zone with 20 wt % solids content and a “free water zone” that contains little solids. This water is recycled as extraction water. Below the free water zone, solids settling continue within the fine tailings; however, the suspension starts to develop non-Newtonian properties which makes further settling an even slower process (Sheeran, 1993). Over 2 to 3 years, fines tailings settle to 30 wt % solids with a stable slurry structure denominated mature fine tailings (MFT). This suspension has very high viscosity and yield stress (Kasperski, 1992; McKinnon, 1989). Further de-watering occurs very slowly and it takes several centuries for the MFT to reach the consistency of soft solids. (Eckert et al., 1996; Sheeran, 1993). Even after 40 years, the MFT do not have enough strength to support the overburden or soil horizon replacement required for reclamation. A schematic cross section of an oil sands tailings pond is shown in Figure 3.5.

Based on these facts, tailings management represents a real environmental impact, primarily related with water usage and recycling. The production of one barrel of bitumen requires approximately 12 barrels of water, where about 70 % of this water is recycled and the remaining 30 % comes from the river, leaving a net requirement of almost 4 barrels or water per barrel of bitumen. This remaining water is tied up in the pore spaces
of the sand, silt, and clay in the tailings, and is effectively lost to the process (Mikula et al., 2008).

It is important to consider that the volume of tailings generated (0.67 m$^3$) is higher than the volume of one tonne of oil sand mined (0.5 m$^3$), and currently, fine tailings and mature fine tailings volumes are increasing at a rate of about 0.1 and 0.06 m$^3$ per tonne of processed oil sand.

Some predictions have established that if the existing tailings management practice continues, the accumulated volume of MFT will increase from the current level of approximately 400 million cubic meters to over one billion cubic meters by the year 2020 (Chalaturnyk et al., 2002). Recognizing the aforementioned numbers, it is very important to manage the tailings disposal and water resources effectively.

**Figure 3.5 Cross section of an Oil Sands Tailings Basin (FTFC, 1995)**

![Cross section of an Oil Sands Tailings Basin](image)

### 3.4.1 Water Chemistry of Fine Tailings

The water in the fine tailings contains a large number of organic compounds, such as naphthenic acids and sulphonates, coming from the bitumen during the extraction process. These acids are responsible for the water toxicity. Moreover, the water contains
a large number of electrolyte species, such as Cl\(^-\), SO\(_4\)^{2-}, HCO\(_3\)^-, Ca\(^{2+}\), Mg\(^{2+}\) and Na\(^+\). Table 3.1 shows a water analysis for different water sources.

**Table 3.1 Water Analysis in River and Syncrude Pond Waters (FTFC, 1995, Vol.IV)**

<table>
<thead>
<tr>
<th>Species</th>
<th>Unit</th>
<th>River water (summer)</th>
<th>River water (winter)</th>
<th>Syncrude pond water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(^-)</td>
<td>ppm</td>
<td>6.0</td>
<td>14.0</td>
<td>136.0</td>
</tr>
<tr>
<td>SO(_4)^{2-}</td>
<td>ppm</td>
<td>26.0</td>
<td>37.0</td>
<td>215.0</td>
</tr>
<tr>
<td>HCO(_3)^-</td>
<td>meq/L</td>
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<td>3.3</td>
<td>14.2</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>ppm</td>
<td>10.0</td>
<td>17.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>ppm</td>
<td>35.0</td>
<td>60.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>ppm</td>
<td>18.0</td>
<td>-</td>
<td>538.0</td>
</tr>
<tr>
<td>Ph</td>
<td>-</td>
<td>7.7</td>
<td>7.7</td>
<td>8.2</td>
</tr>
</tbody>
</table>

The water analysis shows that the calcium and magnesium concentrations are less in the pond water than in the river water because these ionic species are removed when they react with the clays in the oil sand ore and with the carboxylic surfactants generated during bitumen extraction. The high levels of sodium and chloride are due to the soda addition and the processing of the oil sands that contain NaCl in their connate water, in the range of 1.7-5.8 g/l. The concentrations of Na\(^+\) and Cl\(^-\) have shown a 200-300 % increase from 1979 to 1993 (Mikula et al., 1996). The high level of bicarbonate HCO\(_3\)^- arises from the oil sand ore itself, from atmospheric CO\(_2\) absorption and from bacterial activity in the pond.

It is possible to appreciate that optimizing water recycle volumes degrades water quality, possibly reaching to the point where bitumen extraction is not feasible. Therefore, the ions that interfere with the extraction process must be removed through a water treatment, and proper process optimization requires a balance between optimal extraction conditions, and conditions for optimal settling of tailings.
3.4.2 Settling of the Fine Tailings Suspension

Settling of the fine tailings can be divided in three stages: Stokes law sedimentation, hindered settling and consolidation. In the first stage the particles sediment according to their size and relative density, and this approach assumes that the particles do not carry significant surface charges. In the hindered settling, the particles are in close enough in proximity to influence each other and the solids can be considered to be settling as a solid mass or an agglomeration. Finally, in the consolidation stage, a structure is set up so that effective interparticulate stress develops between the tailings particles. Consolidation is controlled by the permeability and compressibility of the system and is induced by the weight of the particles (Shaw et al., 1996). As a result of the consolidation process, excess pore pressure is established in the suspension, which gradually dissipates as the fine tails consolidate and eventually reaches a value of zero in the fully consolidated system. In current tailings consolidation is expected to take centuries (Yong et al., 1984).

Settling rates are usually measured in settling columns where the variation of the height of the solid-water interface with respect to time is measured. Settling columns are not very accurate, however, as the measurement of the interface in a gradually settling system depends on the procedure followed by the operator. In recent years, equipments for directly measuring the interaction forces between colloidal particles has been developed, since the settling of fine tailings is largely determined by the long-range interactions and adhesion forces between the fine clay particles. The surface force apparatus (SFA) and the atomic force microscope (AFM) allow for the study of the effects of chemical addition to a colloid system (Long et al., 2006). However, these apparatuses are generally utilized in laboratories for improvements in fundamental understanding of tailings properties. For onsite applications designed to improve process efficiency, new technologies and equipment are still needed.
3.5 Technologies Developed to Improve Tailings Management

Before 1989, the best available technology to manage mature fine tailings was wet landscape reclamation. Fundamentally, this technology involved transferring the accumulated MFT from the tailing ponds into the mined out area and covering it with a layer of water to create an artificial lake that would sit on top of over million cubic meters of accumulated mature fine tailings.

In 1989, the Fine Tailings Fundamental Consortium was created to develop new tailings management options (Masliyah, 2007). As a result, many other dewatering alternatives have been proposed and the most significant of the options is the consolidated tailings (CT) treatment process commercialized by Suncor in 1994 (Kasperski and Mikula, 1996). A new technology called paste technology is also emerging from efforts made by Syncrude, Suncor, and Albian Sands (Masliyah, 2007). The fundamental difference between these two technologies is that the consolidated tailings process uses gypsum as coagulant while the paste technology uses polyacrylamides of high density as a flocculant.

Fundamentally, coagulation implies the formation of compact aggregates, leading to the macroscopic separation of a coagulum. In this manner, coagulated aggregates of clays can separate very quickly from the original suspension. The drawback of this approach is that significant amounts of water may be trapped within these aggregates, so water recycling may not be as efficient, and the final sediment of sand and coagulated clays may not be as compact as they would be if slower settling of individual particles had been permitted. The process of flocculation implies the formation of a loose or open network, which may, or may not, separate macroscopically (Everett, 1972). Thus, polyacrylamides may lead to a more compact final mixture. Moreover, the effects of combining both flocculant and coagulant are being analyzed.
3.5.1 Consolidated Tailings (CT) Process

The consolidated tailings process is also named as composite tailings by Syncrude, or non-segregating tailings (NST) by Canadian Natural. This is a method where mature fine tailings and a sand slurry are mixed with the goal of the MFT replacing the water found between the grains of the sand slurry. This means that clay particles are packed into the pore spaces of the coarse sand fraction of tailings, allowing the water occupying the sand pores to be released and recovered. Thus, the MFT volume could eventually be located in a sand deposit that could potentially support overburden and vegetation.

This strength of the final mixture of sand and MFT is associated with grain-to-grain contact in the coarse material and with the fluid tailings occupying the pore spaces. In order to obtain an adequate grain-to-grain contact and therefore a deposit that can sustain some load capacity, the volume of the sand pores cannot be less that the volume of the consolidated fine tailings fractions. This implies that there is minimum sand to fines fraction required to create a reclaimable CT deposit. For instance, a slurry is a non-segregating type if it contains 62 wt % total solids and 25 % fines in the solids. Under this composition, all solids settle and consolidate as one unit, consequently, water is quickly released and a consolidated sediment with high solids content is obtained. Conversely, a slurry containing only 45 % total solids with less than 20% fine in the solids would not have a non-segregating characteristic (Masliyah, 2007). In such a mixture, only some of the pore spaces between the sand grains will be occupied by MFT, and thus less water will also be recovered. The formation of non-segregating tailings is therefore a function of tailings solid content, fines content, and fines ratio (wt % of fines of the water and fines fraction).

To achieve this non-segregating phenomenon, it is necessary to develop enough strength in the mature fine tailings so that the mixture can support a sand content from 3 to 5 times the fines content in the mix. If the MFT cannot support the sand enough to induce slow settling, the sand will simply fall through the MFT and will not trap the tailings in its pore spaces. Typically, gypsum (calcium sulphate, CaSO₄·2H₂O) is added as a coagulant to quickly develop enough strength in the MFT to support the sand component while the
fluid phase consolidates. Other process additive options were also considered during the CT process development; these included carbon dioxide (CO$_2$), acid (H$_2$SO$_4$), lime (CaO, Ca(OH)$_2$), acid-lime (H$_2$SO$_4$-CaO), sodium aluminate (Na$_2$Al$_2$O$_3$), alum (48% Al$_2$(SO$_4$)$_3$·14.3H$_2$O), lime-CO$_2$, and organic polymers (polyacrylamides).

Gypsum has been found to be very effective in tailings management because it is a source of Ca$^{2+}$ and early studies have demonstrated that the presence of Ca$^{2+}$ reduces the water soluble asphaltic acids. This reduction in the surfactant concentration leads to an increase in the surface and interfacial tension of the aqueous media, and the clay particles coagulate (Speight and Moschopedis, 1977). In the industry, about 1 kg CaSO$_4$/m$^3$ tailings is used to produce composite tailings by blending MFT and cyclone underflow. Finally, a product with sand to fines ratio of about 5:1 and improved dewatering characteristic is obtained (Chalaturnyk et al., 2002).

The first stage in the CT industrial process is to feed the coarse tailings from the plant to a hydrocyclone with the combined tails stream having a solids content of about 50 wt %. The overflow stream contains little coarse solids and is further processed to recover any remaining bitumen in the stream. The underflow stream contains most of the coarse solids and it has approximately 72 wt % of solids. This stream is combined with gypsum and MFT that are pumped out of the tailing basins. The final slurry stream contains 62 wt % solids and is pumped to a settling basin. Clarified water for recycling is formed within a few days. After 30 days, a fairly consolidated sediment having about 82 wt % solids is formed (Masliyah, 2007).

In general a consolidated mixture with an excess of 80 % solids has enough strength to support a sand cap and can be reclaimed with replacement of the overburden and the original soil horizons (Mikula et al., 1998). This process therefore has the potential to eliminate wet tailings ponds, and could lead to proper land reclamation after the conclusion of a mining operation. The process flow for non-segregating tailings used by Syncrude is shown in figure 3.6.

Figure 3.7 presents the behaviour of the MFT and sand slurry mixture with no additive, perfect and inadequate sand to fines ratio. When a perfect sand to fines ratio is
formulated, the fluid tailings consolidate and occupy the spaces between the sand grains. With no additive, the sand simply drops through the fluid fine tailings; and if there is an inadequate sand to fine ratio, the excess fluid tailings occupy the top of the deposit.

Figure 3.6 Process Flow for Non-Segregating Tailings Process used by Syncrude (Masliyah, 2007)

One of the advantages of the CT process is that the initial mixture can be easily transported because it is a pumpable slurry. However, this is at the same time a disadvantage because the mixture requires fluid containment in order to consolidate and develop sufficient strength for subsequent overburden replacement. Furthermore, the balance of sand availability for dike construction and the sand requirement for CT production is often at odds since the dikes are built from the sand component of tailings. Overall, it has been shown that if it were possible to implement the CT process in all the available fluid fine tailings, the net water lost would be reduced from four to three barrels
of water per barrel of bitumen (Mikula et al., 2008). This would mean significantly more water available for re-use in the plant.

**Figure 3.7 Schematic of the CT Process (Mikula and Omotoso, 2002)**

A concern with the CT technology is the accumulation of Ca\(^{2+}\) in the recovered process water. Significant amounts of gypsum were required to coagulate the MFT stream, and if these divalent cations are present in the process water, they will precipitate the surfactants caused during the initial slurrying of the oil sand. This will hinder bitumen separation from the sand, and will cause a low bitumen recovery efficiency. Therefore, the elimination of the effect of calcium would require an increased NaOH consumption. In addition, the anaerobic reduction of SO\(_4^{2-}\) ions could produce potentially hazardous H\(_2\)S (Chalaturnyk et al., 2002). In recent years, therefore, research has been conducted into the use of alternate chemical aids to improve the CT process.
3.5.2 Paste Technology

Paste technology addresses a methodology to treat fine tailings as they are produced in the plant, instead of the existing mature fines tailings. This method uses polymers of high molecular weight as flocculants since they will generate larger flocs that settle faster and entrap more water than polymers with low molecular weight.

The flocculation ability of polymers depends on their molecular weight, the number of charge points on the polymers, their concentration in the dispersion, solids particle type and the presence of electrolytes, especially divalent ions in the aqueous phase. The most common anionic polymers used as stabilizers and flocculants are carboxylic, sulfonic and partially hydrolyzed acrylamide chemicals.

Polymers can stabilize a suspension of solids by providing electrostatic or steric repulsion, or can attach to the surface of several solids particles to form a bridge between the particles and eventually a floc of the solids particles. Although various flocculation mechanisms are possible, the most important is flocculation by bridging (Hogg, 1999). In this case, optimum flocculation occurs at flocculant dosages corresponding to a particle coverage that is significantly less than complete. Incomplete surface coverage ensures that there is sufficient unoccupied surface available on each particle, to allow for adsorption during collisions of segments of the flocculant chains attached to the particles (Hogg, 1984). In this manner, bridged particles can collide and eventually form a floc of particles with water trapped in the center. This flocculated solid will settle more rapidly than the individual suspended solids.

Previous researchers (Long et al., 2006) have demonstrated that polymers of high molecular weight, medium charge anionic co-polymers of acrylamide and acrylate, such as Percol 727™, at concentrations under 50 ppm, allow for good flocculation of the fine tailings streams coming from the centrifuges and flotation cells. In initial experiments with polymers, fast settling flocs with a turbid supernatant water layer containing about 1.5 wt % solids were obtained at a pH of about 8.5 (Cymmerman
et al., 1999). Further pilot studies included a thickener in the process, which produced an overflow water stream with less 0.8 wt % of solids and an underflow stream having 52 to 65 wt % solids that behaved like a “paste”. The solids in this underflow stream are mostly fines and clays, at a much higher concentration than they would be found in MFT taken from tailings ponds. Based on these results, Cymmerman et al. (1999) suggested a new tailings disposal concept, denominated “Beach and Paste”, in which fine tailings directly from the extraction process and beach run-off streams are combined and introduced to a thickener where anionic polymer is added. The overflow water from the thickener is recycled to the extraction plant and the underflow stream is pumped onto the sand beaches where consolidation takes place over several weeks. A layer of tailings sand can be placed upon the paste to improved consolidation. The results obtained demonstrated that the ability of a flocculant to produce a clear overflow stream and a high solids content underflow stream is dependent on the fine tailings ratio and its pH (Masliyah, 2007). The beach and paste tailings disposal concept is shown in figure 3.8.

Other series of analyses have also shown that the water chemistry results in varying degrees of fine particle dispersion and therefore in its supernatant clarity. Xu and Hamza (2003) reported that in the case of caustic tailings, a small fraction of fines particles remained in the overflow even at higher polymer dosages. Conversely, non-caustic tailings flocculate with a very clear supernatant, even at very low dosages. The optimal pH is therefore strongly affected by the ions present in the water, and by other changing parameters such as the fines ratio in the tailings.

It is possible that very low concentrations of polymer may be successful in flocculating the suspended clay particles and speeding up the settling process, which would reduce the amount of chemical addition required and also possibly reduce the impact of divalent cations in the recovered water. Paste technology therefore has the potential to improve the efficiency of current extraction operations, even if it does not solve the problem of the already existing MFT settling ponds.
3.5.3 Synergy of CT Process and Paste technology

Recent studies have indicated that there is a potential to develop new technologies for oil sand tailings treatment based on the synergy of the polymer and divalent ions, such as calcium or magnesium, meaning that the final tailings management program may contain a combination of both the CT process and paste technology.

Some of the analysis performed so far combine calcium or magnesium ions (0.008 mol /l) with a concentrated polymer solution (2.5 g/l), over a pH range from 3 to 11 (Sworska et al., 2000). It has found that at low pH clays tend to coagulate while in alkaline pH clays form stable suspensions. Therefore, the addition of Ca$^{2+}$ or Mg$^{2+}$ ions is needed in alkaline media in order to destabilize the suspensions prior to the addition of flocculant, since high molecular weight polymers by themselves are not effective in destabilizing dispersed particles at alkaline pH. The effect of the coagulant and flocculant together is reflected in a better clarity of the supernatant (Sworska et al., 2000), which is also balanced by fast solids settling and a final mixture that contains a high degree of solids.
The use of techniques such as the atomic force microscope (AFM), which measures the interaction forces between particles, has shown that the synergic effect of divalent cations and high molecular weight polymer is better in the presence of magnesium than in the presence of calcium. Although, the effect of magnesium on the absorption of the polymer is similar to that of calcium, magnesium appears to be more efficient than calcium in promoting adhesion and consequently in improving settling. In the case of the polymer, an optimum dosage must be found to promote the strongest adhesion. However, this dosage cannot be too high because it could then result in a weaker adhesion or even purely repulsive force profile between fine particles (Long et al., 2006).

Several different mechanisms have been suggested to explain the action of Ca\(^{2+}\) or Mg\(^{2+}\) ions in promoting the action of polymeric flocculants. The electrolytes may reduce the electrostatic repulsion between the clay and the polymer chains by reducing the surface potential or the thickness of the double layer, or both. When this happens, the polymer molecule may approach the surface and become adsorbed by other mechanisms, most commonly hydrogen bonding. Also, the activating cation may be adsorbed by the clay material and act as a bridge for joining carboxylate ions to active sites on the clay surface (Ramachandra, 1980).

3.6 Summary

Oil can be recovered from the oil sands deposits in Northern Alberta through surface mining and in-situ recovery. For bitumen that is located relatively close to the surface, mining has potential to recover significant volumes of oil at a very high process efficiency. The bitumen in these deposits is not in direct contact with the mineral phase because a thin film of water surrounds individual sands grains, which favours the hot water extraction process. Tailings are produced as a by-product of the oil extraction process, and represent an important environmental impact. Tailings management and water recycling are currently treated through techniques such as consolidated tailings (CT) process, paste technology and a combination of both.
Whether the chosen method for tailings management is the CT process, paste technology or a combination of the two, it is unlikely that a single polymer or divalent cation concentration can be identified that will lead to optimal settling under changing plant conditions. The identification of optimal settling has been well discussed in the literature, but these conditions are not static in the plant. The required levels of chemical addition will change as a reflection of varying process water chemistry and the fines content in the tailings streams. Therefore, it is important to monitor the properties of the settled thickened underflow stream, in order to quickly identify when the process conditions need to be changed, and if the resulting change was successful in improving the tailings settling properties.
CHAPTER 4: DEVELOPMENT OF A NMR BIMODAL COMPOSITIONAL DETECTION METHOD TO CHARACTERIZE TAILINGS SAMPLES

4.1 Introduction

Tailings are characterized by having small amounts of highly viscous oil (1-5 wt %), and solids that are suspended in a continuous water phase. In the NMR technique, these two characteristics combined generate difficulties for correctly estimating the amount of oil present in a tailings sample. This is particularly true if the NMR measurement is performed using the same CPMG or pulse parameters to detect both water and oil signals simultaneously.

The main difficulty with using the same pulse sequence parameters to detect both fluid signals is that bitumen has a significantly faster relaxation time ($T_2$) than water, since the high viscous environment restricts the movement of the protons in oil. Water, in contrast, relaxes much more slowly and also requires a longer re-polarization period in between trains. To capture the response from small amounts of oil, the NMR data must be acquired at very fast echo spacings, and in order to improve the accuracy of the signal a high number of trains should also be run. Water does not require as many trains, but it in order to properly capture the signal from water several seconds must be left before the next train can be run. Therefore, if many trains are required to measure the oil signal, the NMR measurement will become prohibitively long, and in practice a compromise would be necessary between the optimal oil signal and the length of the measurement. As a consequence, the oil peak amplitude obtained from these kinds of NMR spectra generally does not correspond well to the real amount of oil present in a sample, and considerable errors may be present in the estimations of fluid content. In order to improve the oil estimation in tailings samples, a new method was developed to detect water and oil signals separately in a short time (approx. 15 minutes). The method was denominated as the “bimodal compositional detection method” because it uses two sets of CPMG parameters for establishing water and oil signals separately.
Each one of the stages followed during the development of this method is explained in this chapter. The reliability of the method was studied through measurements of synthetic and real tailings samples, which will be demonstrated in the next chapters.

4.2 Instrumentation

In this study, two Ecotek NMR tools, operating at a frequency of approximately 1.5 MHz, were used to perform the measurements of water, oil, water/oil mixtures and synthetic samples. The two NMR tools were denominated NMR1 and NMR2. Both machines were designed to be essentially twins of one another, but for sensitive measurements such as tailings it was necessary to identify the effect of different electronics on the resulting fluid content estimations. All measurements were performed at ambient temperature and pressure. Figure 4.1 shows a picture of one of the NMR tools, which contains a probe that holds vials with an outside diameter up to 4 cm.

Figure 4.1 NMR Tool
The decay data generated by the NMR tools was converted into NMR spectra of amplitudes and relaxation time constants using ExpFit®. This software is a new development of the Tomographic Imaging &. Porous Media Laboratory (TIPM) that fits the measured decay data into predefined bins that are equally spaced on a logarithmic scale of relaxation times. It also allows certain fitting parameters to be modified, such as the regularization term or a weighting of the echoes at early times, to obtain specific information from each NMR spectrum or to observe its variations under various assumptions such as higher or lower assumed levels of noise in the measurement.

4.3 Materials

Cold Lake and Athabasca bitumen were the two types of high viscous oils used throughout this research. Their densities were found to be 0.9960 g/cm$^3$ and 1.0198 g/cm$^3$ respectively. These values were measured at 23°C using an Anton Paar DMA 45 digital density meter with a built in thermostat. The viscosities for Cold Lake and Athabasca bitumen at ambient temperature (23°C) were found to be 66,670 mPa·s and 828,450 mPa·s respectively. Although oil sands mining and the subsequent generation of tailings usually involves Athabasca bitumen, the properties of the oil may vary with depth or location in the reservoir. Certain processes also involve the addition of naphtha or other solvents to the bitumen, which could also act to reduce its viscosity. Therefore, there is value to analyzing the NMR response to different ranges of high viscosity bitumen. The results obtained with these two kinds of viscous oil were compared against a conventional oil, which had density and viscosity values of 0.8557 g/cm$^3$ and 7.7 mPa·s respectively, also at 23°C.

Viscosity measurements were made at four elevated temperatures and extrapolated to ambient temperature (23°C) using the Andrade-Guzman-Reynolds equation (Farouq Ali, 2002). All viscosity measurements were performed using a Wells-Brookfield cone and plate viscometer.

Two types of water were used in the generation of synthetic samples: distilled water and brine. The distilled water and the brine had a density of 0.9970 g/cm$^3$ and 1.0012 g/cm$^3$
correspondingly, at 23°C. The brine was supplied by Shell Canada, and had the typical water composition used in industrial oil sands processing: salinity of 1211 ppm, a sodium content of approximately 300 ppm and a calcium - magnesium content lower than 50 ppm.

The solids used were sand and three types of clays. The sand type was Lane Mountain 70, and the clays were illite (B-Clay, IRC), kaolinite (Elmer Kaolin-KRC) and sodium montmorillonite (Wyoming SWy-2Montmorillonite, Na-MRC). Plainsman Clay located in Medicine Hat, Alberta, supplied the KRC and the IRC. These two clays are mined in Troy, Idaho and Ravenscrag, Saskatchewan, respectively. Source Clays Repository in West Lafayette, Indiana supplied the montmorillonite clays. The Na-MRC was mined in Apache Country, Arizona (Chung, 2007).

4.4 Methodology

As mentioned previously, two NMR tools were used during the preliminary set of experiments of this research. The correct location of the sweet spot, or the area with a uniform magnetic field, was verified in both machines in order to improve the accuracy of the results generated. The size of the sweet spot was similar in both machines, thus the same sealed doped water standard could be used in the calibration and tuning of both relaxometers.

Initially, the NMR1 tool was used to measure water and oil signals with the CPMG parameters used in previous studies to determine the level of accuracy in fluid mass predictions. In order to capture the response of both oil and water in this previous work, a fast echo spacing of 0.16 ms was used, 5000 echoes were acquired (the maximum allowed in the software), giving a measurement of 800 ms of decay data. The wait time between trains was 10,000 ms to allow water to re-polarize, and 16 trains were measured in total. The use of these parameters provided a measurement time of approximately 7 minutes, which was used previously in laboratory measurements of water cut (Ding et al. 2004).
With these parameters, the accuracy of the oil mass predictions was poor and also some scatter was observed in the early time decay data. This scatter is not very relevant in the case of water mass predictions since the relaxation time of water occurs at late times. However, in the case of small amounts of bitumen, the amplitude signal is generally obtained at early relaxation times so scatter in these points lead to considerable uncertainties in the determination of the bitumen amplitude. As a consequence the oil content in a sample can be overestimated or underestimated in multiple measurements.

In order to improve the accuracy, particularly in oil mass predictions, several possible changes could be made. The scatter could have been due to a problem in the actual hardware of the NMR, or alternatively the acquisition parameters that had been chosen were possibly not ideal for systems containing small amounts of viscous oil. The first attempt made for improving the oil mass predictions therefore involved an investigation of different sets of CPMG parameters. Predictions of oil and water mass fractions were analyzed under different pulse parameters and finally two new sets of CPMG parameters were established to determine water and oil signals separately. The method using these two sets of pulse parameters was denominated the “Bimodal Compositional Detection Method”.

The determination of the new CPMG parameters and other measurements were performed initially in the NMR1 tool, and it was determined that this approach did in fact lead to some improvement in the oil mass predictions. However, even with optimized CPMG parameters, there was still scatter in the first few echoes of the NMR decay curve. At this point, the NMR1 machine was sent back to the manufacturer for an upgrade to its electronics, and testing was continued on the sister machine, NMR2, which had already undergone upgrades in the electronic hardware. This approach was followed to identify the effect of the machine hardware on the NMR predictions, specifically to see if there was an effect of the machine in terms of stability of the signal to noise ratio (SNR) of the measurement when small amounts of viscous oil were measured. The second machine did in fact appear to yield more stable spectra, at a higher signal to noise ratio. This led to an important finding: for oil content measurements in samples containing very low amounts
of viscous bitumen, even with optimized acquisition parameters the predictions will still be very sensitive to the electronics and the settings of the NMR machine. This was never an issue before in previous work where the fluids being investigated contained a higher fraction of oil (Bryan *et al.*, 2006, Nui *et al.*, 2006).

After it had been observed that the oil content predictions were highly dependent on the tuning and electronics of the machine, a more detailed calibration was performed on NMR2 using an oscilloscope to further improve the stability and functioning of the NMR electronic equipment. Although the synthetic and real tailings samples tested were measured after all the tuning had been performed on NMR2, the results generated in both machines are shown in this chapter to demonstrate the importance of the stability of an NMR tool in the measurement of tailings samples that contain small amounts of bitumen.

Subsequently, oil and water samples in the properly calibrated NMR tool were measured in order to establish the amplitude indexes (AI) for the two qualities of water and oil that were used in the subsequent analyses. The average absolute errors in mass predictions and the minimal detection limits of the NMR tool for the four substances were also determined. These measurements were performed using samples of oil or water alone.

Afterwards, mixtures of oil and water were measured to analyze variations in the NMR spectra, and to demonstrate that AI values established using water or oil alone could also be used in the determination of fluid masses in samples containing both oil and water. Then, mixtures of water with each one of the principal solids were also studied to establish the stability of the water amplitude indexes under the presence of different clays, and to identify if water content can still be accurately determined even when the water is relaxing more quickly due to surface relaxation with the solids. The stability of the water amplitude index is important because the water mass predictions are calculated based on this value; therefore, it was necessary to confirm if the interactions between water and clay would influence this number significantly.
The samples used in this thesis were all measured at multiple times in the NMR tool. The mass errors presented are the maximum values found during these measurements. Absolute errors are reported because the NMR mass predictions were not consistently high or low.

Each one of the stages mentioned in this methodology is explained in detail in the following sections.

4.5 Sweet Spot Location

The first step to properly using the NMR tools was to perform an adequate tuning and calibration of the hardware and electronics. To begin with, the sweet spot had to be identified, so that all tests would be performed in this region. The sweet spot is the region of uniform field properties in the magnet of the NMR tool. It is very important to locate the proper sweet spot because this region has the strongest signal, which helps to improve the accuracy of NMR predictions.

The sweet spot was found by measuring the amplitude of a fixed-volume sample with a known relaxation time, at different regions of the magnet. The standard sample is denominated doped water and it is a mixture of distilled water and copper sulphate (CuSO₄). Tests could have been done with any fluid that contains a known relaxation time; but doped water was used in this study simply because it behaves as a single exponentially decaying fluid but relaxes much faster than water; thus allowing for faster measurements.

The doped water was placed into a Teflon vessel that has the same diameter as the borehole of the magnet (3.8 cm), and a length of 1 cm. The volume of the sample is therefore approximately 11 cm³, and its length allows for measurements of the amplitude to be obtained at 1 cm intervals along the length of the borehole. Figure 4.2 shows the amplitudes values obtained in the NMR2 tool at different regions or lengths of the magnet, and the center of the sweet spot where the probe or the sample must be located.
When the fluid was outside of the range of the magnet, there was no measurable amplitude. As the fluid moved into the range of constant magnetic strength, the recorded amplitude increased. In the sweet spot, the amplitude would remain relatively constant, since the magnetic field was homogeneous in this region. From figure 4.2 the sweet spot was found to be approximately 3.5 cm in length; therefore, samples of this length can fit entirely within this region of high magnetic field strength. Outside of the sweet spot, the magnetic field and the measured amplitude of the doped water, decreases rapidly to zero. Consequently, the samples in this study were placed in vials that were only 3.5 cm in length. Longer samples would fall outside the sweet spot, and the fluid in these regions would not be measured at the same strength of signal.

Figure 4.2 Location of the Sweet Spot of the NMR Tool

4.6 Calibration of the NMR Tool

Once the sweet spot was located, the samples were always measured in this zone. The next step was to calibrate the NMR tool using also a sealed doped water standard, which had to be done before measuring any actual samples. The typical water relaxation time
for this standard is 20 ms, which again reduces the calibration time, compared to measurements of slower relaxing pure water. The vial was sealed to prevent water evaporation. The use of this standard allowed for the measurements taken on different days to be normalized against one another.

From early measurements with the sealed doped water standard, it was observed that it was necessary to manually fine tune and calibrate the frequency of the electronics and the pulse lengths to acquire the data in the CPMG sequence. This manual calibration of the hardware was necessary because the automated tuning software supplied with the machine led to the generation of noise in the first few echoes, which are very important in the determination of the proper oil amplitude.

The lengths of the pulses were fine-tuned using a digital oscilloscope in order to maximize the value of the signal to noise ratio. Initially, the oscilloscope was grounded for safety considerations and for ensuring accurate measurements. Table 4.1 presents the CPMG parameters selected to perform the calibration process. These parameters were chosen in order to obtain a response on the oscilloscope that would be fast and easy to measure. A large echo spacing (3 ms) allowed for visual identification of the shape of the measured echoes, and 2000 ms had to be left between the trains to allow for full re-polarization of the protons in the standard. Each experiment was run with only 5 echoes and 10 trains in order to obtain a relatively fast measurement, so that the effect of changing the pulse lengths or the magnet frequency could be quickly identified.

<table>
<thead>
<tr>
<th>CPMG Parameters</th>
<th>Values</th>
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<tbody>
<tr>
<td>Time to echo (ms)</td>
<td>3</td>
</tr>
<tr>
<td>Number of B pulses</td>
<td>5</td>
</tr>
<tr>
<td>Wait time (ms)</td>
<td>2000</td>
</tr>
<tr>
<td>Number of trains</td>
<td>10</td>
</tr>
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</table>

During the NMR calibration, the frequency (MHz) and the width of A and B pulses (ms) were the parameters modified. The A and B pulses reorient the spin axes of the hydrogen
nuclei by an axial rotation of 90° (π/2) and 180° (π), respectively. Although a variety of pulse sequences can produce an echo signal, the strongest echo is produced by a 90°-180° (π/2- π) pulse sequence (Stoltenberg, 2006).

The first step in the calibration process consisted of modifying the frequency of the oscillating signal, while keeping the lengths of the A and B pulses constant. An optimal magnet frequency corresponds to the condition where each pulse would lead to a corresponding echo, equally spaced, with no signal in between the echoes. The range used to modify the frequency was found by visual trial and error measurements using the oscilloscope. The main criterion for selecting the correct frequency was the observation on the oscilloscope of the right and left side of the sine waves over a line base. At the optimal magnet frequency, all sine waves had to be over this base line and neither of their lateral sides could present large oscillations. Figures 4.3 to 4.6 show four schemes of the possible signals that can be obtained with different magnet frequencies. The frequency near to resonance, or the ideal case, is represented in figure 4.3 where the pink line is the base line. Examples of distorted sine waves signals that were found during the calibration are presented in figures 4.4 to 4.6. Distorted frequency values correspond to conditions where the signal extends below the base line (figure 4.4), other peaks are generated in between the echoes (figure 4.5) or the echoes are not evenly spaced (figure 4.6). The sine wave signal obtained during the calibration process was similar to figure 4.3, with only minor oscillations at the right and left side. The best frequency value obtained during the calibration process was 1.5026 (MHz).

After having found an adequate frequency value, the A and B pulse lengths were then modified. Theoretically, the A pulse should be exactly half the value of the B pulse, in order to generate an angular rotation of 90°, compared to 180° for the B pulses (Stoltenberg, 2006). In practice, the relationship between the A and B pulse lengths may not be exact due to the electronics in the instrument.

Initially, the A and B pulses were set to be the same value. Without an initial 90° pulse to flip the protons onto the transverse plane, where the signal is being measured, there
should be essentially no signal. Thus, with both A and B pulses set to the same value, the B pulse lengths were optimized by finding the value where the resulting signal was minimized. This was observed as small and continuous sine wave signals, which were very close to each other and had very low amplitude. The best value found for B pulses was 0.044 ms. Subsequently, the value of A pulses was set to half of the B pulse value and then fine-tuned to ensure an axial rotation of 90°, which would then maximize the signal. The best value found for these pulses was 0.023 ms. As expected, this value was close to, but not exactly, half of the length of the B pulses. A representation of the behaviour of the A and B pulses is shown in figure 4.7, where it is possible to observe an initial A pulse, followed by spin echoes located between the B pulses (Stoltenberg, 2006).

It is important to mention that even after fine-tuning, some remaining noise was still present in the NMR signal since the calibration was performed with the electronics exposed to the environment, and there may be some minor changes in the signal when the NMR tool is completely closed. Additionally, fine-tuning of the electronics was a visual trial and error approach, and required knowledge of what the various parameters such as the magnet frequency and the pulse lengths mean. While this first step is required for accurate NMR measurements of tailings, plant operators would not be expected to perform this fine-tuning. Rather, the machine should be properly tuned before setting it up in a plant or laboratory, and after the parameters have been fine-tuned it can then be run normally.
Figures 4.3 to 4.6 Schemes of the Signals for Different Oscillator Frequencies

Figure 4.3 Frequency Near to Resonance  
Figure 4.4 Distorted Frequency  
Figure 4.5 Distorted Frequency  
Figure 4.6 Distorted Frequency
4.7 Development of a Bimodal Compositional Detection Method

Sections 4.5 and 4.6 detailed the fine-tuning and calibration of the machine hardware. In order to properly measure the response from tailings samples, further optimization of the acquisition parameters was also required. As mentioned previously, NMR pulse parameters designed to capture the responses from both oil and water in a single NMR measurement could not provide accurate estimates of oil content in tailings samples. This study therefore presents a deviation from previous approaches, in that oil and water signals are determined separately, in multiple NMR measurements. In this manner, optimized measurements for estimating water content and oil content can be performed in relatively short times: approximately 15 minutes.
4.7.1 Establishment of CPMG Parameters to Detect Water Signal

Initially, different amounts of distilled water (0.5 – 12 g) were measured in the NMR1 tool to establish the amplitude index of water through mass balance. The first parameters used were similar to those used in previous research (Ding et al., 2004). However, the correlation between the water masses and their amplitudes indexes did not result in a perfect straight line. In order to improve this relationship, the number of trains or repetitions was increased from 16 to 26, which should statistically allow for a better accuracy of the results since the final decay curve would now be the result of a higher number of individual trains. The time spent during one NMR measurement using 16 and 26 trains is approximately 7 and 10 minutes correspondingly. Table 4.2 shows the previous and new CPMG parameters used to detect water signal.

Table 4.2 Previous and New CPMG Parameters Used to Detect Water Signal

<table>
<thead>
<tr>
<th>CPMG Parameters</th>
<th>Previous</th>
<th>New</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time to echo (ms)</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>Number of B pulses</td>
<td>5000</td>
<td>5000</td>
</tr>
<tr>
<td>Wait time (ms)</td>
<td>10000</td>
<td>10000</td>
</tr>
<tr>
<td>Number of trains</td>
<td>16</td>
<td>26</td>
</tr>
</tbody>
</table>

Figure 4.8 and 4.9 show the straight lines obtained from the correlation between the amplitude data and different amounts of distilled water. The slopes obtained from this figures are the amplitude index values for water. These values were found to be 0.1607 and 0.1656 in the case of 16 and 26 trains respectively. As expected, the values were similar (different only in the third decimal place) since in general water is an easy substance to measure even with fewer trains. However, the average absolute error in the water mass predictions in the NMR1 tool was ± 0.21g and ± 0.17g using the previous and new CPMG parameters, in that order. It is notable that the error in the water mass predictions was reduced with the larger number of trains, especially for lower water masses. Based on these results, the number of trains selected to detect the water signal during all the experiments of this research was fixed at 26.
The amplitude indexes for water and brine were also determined using the NMR2 tool, which had its electronics fine-tuned and calibrated using the oscilloscope. The amplitude indexes obtained in this machine using 26 trains for distilled water and brine were 0.1424 and 0.1453. These values are shown in figures 4.10 and 4.11. It had been demonstrated that in extremely saline brines this factor may change (Chung, 2007); however, the similarity of these values shows that the low salinity of the water in the plant does not have a significant effect on the water amplitude index value. The average absolute error found for water and brine mass predictions were 0.12 g and 0.11 g, and the minimum detection limit for both qualities of water was established as 0.5 g.

Figure 4.8 Amplitude vs. Mass of Distilled Water Using a Number of Trains Equal to 16, NMR1 Tool

Figure 4.9 Amplitude vs. Mass of Distilled Water Using a Number of Trains Equal to 26, NMR1 Tool
Figure 4.10 Amplitude vs. Mass of Distilled Water Using a Number of Trains Equal to 26, NMR2 Tool

Figure 4.11 Amplitude vs. Mass of Brine Using a Number of Trains Equal to 26, NMR2 Tool

\[ y = 0.1424x \]
\[ R^2 = 0.9995 \]

\[ y = 0.1453x \]
\[ R^2 = 0.9993 \]

Figure 4.12 shows the NMR spectra for 3 g of distilled water and brine. Both qualities of water relaxed at around 2000 ms, as expected, since for this low salinity brine the viscosity of distilled water and brine were the same. The fact that water relaxes so slowly allowed for a definition of 1000 ms as the cut off for bulk or free water. The spectra obtained for other amounts of water showed that greater substance masses correspond to bigger amplitude peaks. In all cases the water signal occurred at the same relaxation times (T2), as related to the low viscosity of the water (Coates et al., 1999).

Overall, the NMR2 tool gave better and more consistent results than NMR1, and the difference in water amplitude indexes between the two machines can be attributed to differences in the NMR electronics. For optimal measurements of fluid volumes, proper tuning and optimization of the machine hardware are therefore vital to this application. Once the hardware has been optimized, the water measurements can then be optimized through an identification of pulse parameters that provides a stable water measurement within a reasonable time.
4.7.2 Establishment of CPMG Parameters to Detect Bitumen Signal

Cold Lake and Athabasca bitumen were the two types of unconventional oil analyzed in this study. As in the case of water, the NMR1 tool was initially used to perform the measurements in order to determine the accuracy in the bitumen mass predictions, with the parameters used in previous research. These parameters are presented in table 4.3, along with new parameters that were designed to give a better oil response. The “New” parameters were identified after comparing the results of predictions of oil mass obtained under multiple parameter choices.

**Table 4.3 Previous and New CPMG Parameters to Detect Bitumen**

<table>
<thead>
<tr>
<th>CPMG Parameters</th>
<th>Previous</th>
<th>New</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time to echo (ms)</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td>Number of B pulses</td>
<td>500</td>
<td>200</td>
</tr>
<tr>
<td>Wait time (ms)</td>
<td>1000</td>
<td>100</td>
</tr>
<tr>
<td>Number of trains</td>
<td>100</td>
<td>1000</td>
</tr>
</tbody>
</table>

The initial amounts of Cold Lake bitumen measured in the NMR1 tool varied from 0.2 to 13 g. As previously mentioned, measurements were first made using the original, or “Previous”, oil pulse parameters. The correlation obtained between amplitudes and mass
values was good in general, as can be observed in figure 4.13. It should be noted, however, that a significant deviation was observed when the amount of oil present was less than 3.5g (figure 4.14). This deviation or inaccuracy in the oil mass predictions is due mainly to the high viscosity of oil that restricts the movement of its protons and generates oil peaks with faster relaxation times. The result is that for small amounts of oil, it becomes difficult to accurately capture the fast decaying oil signal and separate this signal from possible noise in the first few echoes, so the amplitudes values do not correspond to the real amount of oil present in a sample. This fact meant that in order to capture a better oil signal the CPMG parameters were required to be modified and this was particularly true for tailings, where the oil content is usually small. For this reason, a new set of CPMG parameters was established.

As can be observed in table 4.3, the pulse parameters modified to improve the oil signal detection were the number of B pulses, the wait time and number of trains; the echo spacing was kept constant at the fastest possible value for these machines (0.16 ms). Viscous bitumen relaxes very quickly, so fewer echoes are required to capture the signal
from the oil. In addition, since the oil relaxes so quickly, the re-polarization time will also be short, and could thus be reduced from 1000 ms down to 100 ms. NMR theory states that, in general, the re-polarization time only needs to be 3 - 5 times the $T_2$ relaxation time of the fluid being measured (Coates et al., 1999). For viscous bitumen, that relaxes under 10 ms, 100 ms was allowed for re-polarization in order to ensure that the protons were fully re-aligned with the static magnetic field.

This faster experiment allowed for more trains to be run (1000 trains instead of only 100 trains), thus improving the statistical accuracy of the measurement, since once again the final decay curve was the result of 1000 individual measurements instead of only 100. Although the number of trains or repetitions was significantly increased in the new pulse parameters, a measurement of a sample using these parameters takes only around four minutes because the number of pulses and the wait time between trains had been reduced. A higher number of trains (1500 trains) was also tested, but it was observed that this longer measurement did not lead to any further improvement in the oil content predictions. It is notable that due to the difference between the NMR relaxation times of oil and water, most of the CPMG parameters to detect the oil signal were modified.

Having defined the “New” CPMG parameters, the same Cold Lake bitumen samples were measured again in the NMR1 tool. The correlations among amplitudes and masses obtained with these parameters provided better results; however a deviation was still observed for amounts of oil less than 3.5g. The results for Cold Lake samples are shown in figures 4.15 and 4.16. This deviation was smaller than the original correlation shown in figure 4.14, indicating that these new parameters were in fact better for predicting bitumen mass in low oil content samples.

Samples containing up to 6 g of Athabasca bitumen were also measured in the NMR1 tool, and the correlation among amplitudes and masses for this type of oil is shown in figure 4.17. The average absolute errors in oil mass predictions for Cold Lake and Athabasca bitumen samples were 0.23g and 0.14g, in that order.
Figure 4.15 Amplitude vs. Mass of Cold Lake Bitumen (0.2 to 13 g) Using New CPMG Parameters, NMR1 Tool

Figure 4.16 Amplitude vs. Mass of Cold Lake Bitumen (0.2 to 3 g) Using New CPMG Parameters, NMR1 Tool

Figure 4.17 Amplitude vs. Mass of Athabasca Bitumen Using New CPMG Parameters, NMR1 Tool
Having found that the NMR1 tool was capable of detecting large amounts of oil and that the new parameter choice led to smaller errors in the oil content predictions, the next set of measurements was performed in the calibrated NMR2 tool using oil samples containing only 0.5 to 6 grams of Cold Lake and Athabasca bitumen. Small oil masses were specifically chosen since the oil amount present in a tailings sample is low. The mass predictions found for both types of bitumen had an average absolute error of 0.09 g; which is a better result than those obtained with the NMR1 tool. This was evidence that for samples with low oil content, the process of minimizing the noise in the NMR signal through both hardware and acquisition or pulse parameter improvements is extremely important to the application of this technology for oil content determination. Amplitude indexes equal to 0.1152 and 0.0650 for Cold Lake and Athabasca bitumen were found from the slopes in figures 4.18 and 4.19 respectively. The fact that the Athabasca bitumen had a lower amplitude index is related to the higher oil viscosity (Bryan et al., 2005).

The NMR spectra for 1.5 g of each type of bitumen are shown in figure 4.20. From these spectra it is possible to observe that both viscous bitumens relax before 10 ms, which is distinctly different from water. This relaxation time allows for a definition of the upper limit cut off for bitumen: any signal above 10 ms will definitively not be the contribution of bitumen. In addition, it is notable that Athabasca bitumen has less amplitude and a shorter mean relaxation time than Cold Lake bitumen because of its higher viscosity; consequently, NMR detection of this type of bitumen is more difficult. According to figures 4.18 and 4.19 the minimal oil detection limits for both types of bitumen, conserving a good level of accuracy, was determined as 0.6 g. This is higher than the detection limit of water, and is due to the fact that viscous bitumen is more difficult to measure than water.
In order to verify that the high viscosity of bitumen really affects the accuracy of the NMR mass predictions, samples containing amounts from 0.5 to 6 g of conventional oil (viscosity 7.7 mPa·s at 23°C) were measured. Figure 4.21 presents a perfect fit among the masses and their amplitudes, which demonstrates that the NMR2 has a high signal to noise ratio and that the high viscosity of bitumen really affects the accuracy in oil mass predictions. The average absolute error found in mass predictions was 0.3 g, which is significantly lower than the errors in the bitumen masses. A comparison among the NMR spectra for 0.6 g of the three kinds of oils is shown in figure 4.22. Here, it is apparent that the conventional oil sample is much lower viscosity, since the oil peak is close to 100 ms and the amplitude is larger, for the same mass of oil.
Figure 4.20 NMR Spectra for 1.5 g of Cold Lake and Athabasca Bitumen

Figure 4.21 Amplitude vs. Mass of a Conventional Oil Using New CPMG Parameters, NMR2 Tool
4.8 Analysis of Water and Bitumen Mixture

Mixtures of water and bitumen were prepared containing the two qualities of bitumen and water and were measured using the new CPMG parameters. The initial mixtures were prepared with different amounts of bitumen ranging from 0.6 to 6.0 g and approximately 10 g of water in each sample. These samples therefore had oil contents ranging from 5 - 37.5 wt %. The first set of samples was prepared with Cold Lake bitumen and distilled water, and in the second set of samples Athabasca bitumen and plant brine were used. In both cases the oil was added first, and then water was placed on top of the oil. Due to the difference in density, the oil could then float to the top of the water.

Each sample was measured using the parameters to detect the oil and water signals separately at 0 and 48 hours in the NMR1 tool. The oil and water measurement took approximately four and ten minutes respectively; consequently, a complete measurement of each sample in a NMR tool required approximately 15 minutes.
Figure 4.23 shows the spectrum generated using the parameters to detect oil signal for the mixture of 0.6 g of Cold Lake bitumen with 10 g of distilled water at 0 and 48 hours. The results for the mixture of Athabasca bitumen and brine are illustrated in figure 4.24. These spectra show well-defined peaks below 10 ms for the small amount of bitumen used. Due to small amounts of noise below 10 ms, a fixed cut off could not be applied; rather oil was taken as the amplitude up to the end of the first peak. The 10 ms cut off was still used as the upper limit, however; any signal above 10 ms was known not to be oil. An additional observation made from these samples was that the oil signal would begin close to or before 1 ms. Therefore, if a given measured amplitude peak is to be attributed to bitumen, it should begin close to or before 1 ms, and should end before 10 ms.

Figures 4.25 and 4.26 present the spectra for the same mixtures, but using the parameters to detect water signal. The water peaks in these spectra were also well defined after 1000 ms; this value was used as the cut off for water mass calculation. The average absolute errors found in water mass predictions were 0.3 g and 0.15 g for Cold Lake and Athabasca mixtures respectively. In the case of oil mass predictions, the errors were 0.6 g in both cases. As expected, when the oil content was very low, the resulting error in the oil mass prediction could be significant.

Tailings samples were eventually analysed using NMR2; the results of the oil/water mixture measurements were simply obtained to serve as an illustration of the approach used to determine the fluid content separately, through multiple measurements on the same samples.
Figure 4.23 NMR Spectra of Cold Lake Bitumen and Distilled Water Mixture Using Parameters to Detect Oil Signal

Figure 4.24 NMR Spectra of Athabasca Bitumen and Brine Mixture Using Parameters to Detect Oil Signal

Figure 4.25 NMR Spectra of Cold Lake Bitumen and Distilled Water Mixture Using Parameters to Detect Water Signal

Figure 4.26 NMR Spectra of Athabasca Bitumen and Brine Mixture Using Parameters to Detect Water Signal
4.9 Analysis of Water and Solids Mixture

Fine tailings normally consist of water from 58 to 62 wt % and 37 wt % of solids. The solids generally consist of a clay content of approximately 95 wt %, and the other 5 wt % is sand. Kaolinite, illite and sodium montmorillonite are the three main types of clay present. The high clay fraction in tailings makes it important to study the behaviour through time of each clay type mixed with water or brine. Spectra analysis of each mixture allows for the determination of typical relaxation times and the swelling capacity of each clay. The importance of these measurements was to identify if signals at very early times could still be taken to be the contribution from oil, or if the oil and clay bound water signals would begin to overlap. In order to determine the clay response, the three typical clays were mixed separately with distilled water and brine in a proportion of 50/50 wt %. Based on the typical tailings composition, a synthetic tailings sample of 20 g contained 7.4 g of water; thus, the amount of clay added to each sample was also 7.4 g. To make these samples, water was added to dry clay at 0 hours and soaked into the clay over a 24 hour period.

Figures 4.27 to 4.32 show the spectra obtained for kaolinite, illite and sodium montmorillonite mixed with distilled water and brine at 0 and 24 hours using the parameters to detect water signal. The spectra of kaolinite and illite mixed with both types of water looked very similar to one another. Both clays showed relaxation times around 10 to 100 ms. In contrast, montmorillonite spectra exhibited a faster relaxation for both 0 and 24 hours. This phenomenon was especially significant for the distilled water sample, and may be attributed to a higher swelling capacity of this clay in the absence of salt.

Spectra of kaolinite and illite presented a peak after 1000 ms that corresponds to free water; the other peaks between 10 and 100 ms represent the effect of surface relaxation or available solids surface (Hum, 2005). After 24 hours, all spectra showed faster relaxation, indicating that the movement of water into small pores appeared to be a time-dependent process, as air had to be displaced out of the clay while water imbibed in.
The difference between illite/kaolinite and montmorillonite is evident both in the short and long $T_2$ values. When the clay was montmorillonite, there was no bulk water peak present even at 0 hrs, even though the initial mixture had contained 50 wt % of water. This indicates the clay structure had swelled, and all the water was now associated with surface relaxation. In addition, the water relaxation times were predominantly under 10 ms at 0 hrs, but the water relaxed more slowly after the fluids had been allowed to redistribute for 24 hrs. This is opposite to the behaviour of illite and kaolinite. These spectra also illustrated that the relaxation times for water bound to clay were not always greater than 10 ms; consequently no single cut off $T_2$ value could be assumed for the fraction of clay bound water present in the samples.

In the absence of bitumen all amplitude data were related to water, so the total amplitudes were used to predict water content in these kinds of mixtures. When small amounts of bitumen are present the oil and clay bound water relaxation times are similar, which makes separation difficult (Bryan et al., 2006). In general, however, several conclusions could be made. If the clay is predominantly illite or kaolinite, the relaxation times even for surface bound water do not begin until close to 10 ms, and end at around 100 ms. If the sample contains significant montmorillonite, however, the relaxation times for water can overlap with that of the bitumen. Therefore, when significant montmorillonite is present, NMR predictions of oil and water content will be less accurate.
Figure 4.27 NMR Spectra of Kaolinite and Distilled Water Mixture

Figure 4.28 NMR Spectra of Kaolinite and Brine Mixture

Figure 4.29 NMR Spectra of Illite and Distilled Water Mixture

Figure 4.30 NMR Spectra of Illite and Brine Mixture
Water mass prediction for kaolinite and brine mixture had an absolute error of 0.24 g at 0 and 24 hours. The mass prediction error for illite and brine mixture was 0.14 g, again both at 0 and 24 hours. The water mass predictions for these mixtures using distilled water had errors of 0.12 g at 0 hours but the error was greater than 0.5 g at 24h. This may have been due to differences in the clay-water interactions in the absence of salt, or was possibly related to instability in the NMR1 machine.

The results for sodium montmorillonite and brine mixture were less accurate. This could be attributed to higher iron content in this clay that could affect the signal given by NMR tool, or the measured water content may have been incorrect due to additional water that already existed in the clay matrix (Chung, 2007). If the clay is predominantly montmorillonite then the NMR water content predictions will therefore tend to be less accurate. However, in general this clay type does not have a significant effect on the synthetic tailings measurements because its proportion in clay content is less than 5 wt % (Shaw, 1996). Therefore, the uncertainties associated with water content in montmorillonite, and the water relaxation times for this clay, will generally not cause significant problems in the measurement of tailings samples.
As mentioned previously, sand constitutes approximately 5 wt % of the solid content in a tailings sample. Thus, distilled water and brine were mixed separately with sand in the same proportion used with the clay mixtures. Figures 4.33 and 4.34 show the spectra for sand with distilled water or brine at 0 and 24 hours. The relaxation time found for sand was in the range of several hundred milliseconds, only slightly faster than the signal from bulk water. In the absence of confining pressure, the pore spaces are in sand grains are much larger than in clays, leading to slower relaxation. Previous studies have shown that the presence of sand does not have a significant effect on the amplitude index of water (Chung, 2007), and this was also verified in this work. The average absolute error for the mixtures containing sand and brine was 0.19 g, and for the mixtures prepared with distilled water was 0.03 g.

Figure 4.33 NMR Spectra of Sand and Distilled Water Mixture

Figure 4.34 NMR Spectra of Sand and Brine Mixture
4.10 Analysis of Water and Kaolinite - Illite Mixture

After having studied the behaviour of each solid mixed separately with water or brine, the stability of the water amplitude index through time was verified when brine or water was mixed with both of the two typical clays found in the greatest proportions in the tailings. The stability of the water amplitude index is important because any variation in this value through time directly affects the water mass prediction in a sample. Any systematic changes in amplitude index will be due to chemical interactions between the clay and water or brine, while random fluctuations are a reflection of the machine stability.

The typical kaolinite and illite content in a tailings sample is 35 wt % and 60 wt % of the clay fraction, respectively (Shaw, 1996). Thus, seven samples of 20 g were prepared containing a solid phase consisting of 60 % illite, 40 % kaolinite, and distilled water ranging from 40 wt % to wt 70 % of the total sample mass, in intervals of 5 wt %. Another seven samples were prepared with brine and the same clay proportions. All samples were analyzed at 0, 24, 48, 96 hours and one week later in the NMR1 tool.

In figures 4.35 and 4.36, the fluid mass is plotted against the NMR amplitude for the various samples at each of the times measured. The slope of the line is the amplitude index of the water or brine. It is evident that the brine amplitude index remains constant even after one week with an average value of AI = 0.1670. The same stability was obtained for the mixtures using distilled water and their amplitude index found was AI = 0.1688. The average error in the water mass predictions was found to be 0.49 g and 0.60 g for brine and distilled water, respectively. The amplitude index values are essentially the same as those obtained with measurements of water alone using the same machine (NMR1), thus these tests showed that the mixture of kaolinite and illite with water or brine does not affect the water and brine amplitude indexes over time. In this manner, NMR predictions of water content in tailings samples should be valid both at early times to monitor conditions in the plant or after the tailings have already settled for extended times in ponds.
4.11 Summary

A bimodal compositional detection method was developed to improve prediction of fluid content for the range of values typical of tailings. This method consists of using different acquisition parameters to detect water and oil signals separately. The main reason to develop this new method was that the small amounts of highly viscous oil present in tailings samples cannot be easily detected by the NMR tool, using the typical parameters to detect the water signal. The measurement of a sample using this method takes approximately fifteen minutes.

During the development and evaluation of this method, two qualities of water and bitumen were used to prepare the synthetic samples. Each type of water and bitumen was analyzed as a single substance and in a mixture. The amplitude indexes of both qualities of water and oil were determined. In addition, the NMR detection limits for water and oil were found to be 0.5g and 0.6 g correspondingly.
Moreover, both types of water were mixed with the typical solids found in tailings composition (kaolinite, illite, sodium montmorillonite and sand) in order to verify that the amplitude index of water does not change significantly in the presence of these solids, which could affect the water mass predictions. Based on these results, tailings synthetic samples were prepared and analyzed using the new method. Subsequently, real tailings samples were also provided for analysis with the new methodology. The results obtained for these samples using the bimodal compositional detection method are presented in the following chapters.
CHAPTER 5: ANALYSIS OF SYNTHETIC AND REAL TAILINGS SAMPLES

5.1 Introduction

At this stage, the stability of the NMR tool had been tested for pure samples and mixtures of bitumen/water and water/solids. The next step was to determine if accurate predictions of fluid content could be made using synthetic tailings samples, containing known masses of oil, water and solids. Subsequently, actual middlings and tailings samples were prepared in a batch extraction unit (BEU) in the Shell Canada Research Centre. These samples were also analyzed through the NMR technique using the bimodal compositional detection method, and were named real tailings samples.

5.2 Analysis of Synthetic Tailings Samples

Synthetic samples of 20 g were prepared using typical fine tailings compositions. The mixing configuration was the main parameter varied in these samples. The methodology used was to create two large groups depending on the oil and water used, and then to subdivide each group into three smaller groups titled Test One, Test Two and Test Three. Each small subgroup had five samples, comprising fifteen samples in total per main group. In the first group, Athabasca bitumen and brine were used, while Cold Lake bitumen and distilled water were the fluids used in the second group.

The samples of the both groups were measured in the NMR2 tool, which had previously been fine-tuned. The five samples of each subgroup contained bitumen from 1 to 5 wt %, water from 58 to 62 wt %, and 37 wt % of solids. This means that the first sample contained 1 wt % of oil, 62 wt % of water and 37 wt % of solids. The second sample contained the same solids percentage, but 2 wt % of bitumen and 61 wt % of water, and so on with the other samples. The fixed solids component in these samples was a mixture of clay (< 22 μm) and sand (> 22 μm) that was prepared prior to each test. The solids consisted of 95 wt % of clay and 5 wt % of sand. Illite (60 wt %), kaolinite (35 wt %) and sodium montmorillonite (5 wt %) were the three type of clays used to prepare the clay.
fraction since these are the three main clays found typically in the fine tailings. The weight fractions of the various clays were also decided based on typical tailings compositions (Mikula, 1996). The goal of these measurements on synthetic samples was therefore to validate the accuracy of the bimodal compositional detection method, using known amounts of fluids in quantities that are representative of actual tailings.

The amounts of each substance used in the preparation of the samples for the three tests are presented in Table 5.1.

Table 5.1 Mass Compositions of Tailings Synthetic Samples Used During the Three Tests

<table>
<thead>
<tr>
<th>Mass Fraction (g) and % Bitumen</th>
<th>1 %</th>
<th>2 %</th>
<th>3 %</th>
<th>4 %</th>
<th>5 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bitumen 0.2</td>
<td>0.4</td>
<td>0.6</td>
<td>0.8</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Water 12.4</td>
<td>12.2</td>
<td>12</td>
<td>11.8</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>Sand 0.37</td>
<td>0.37</td>
<td>0.37</td>
<td>0.37</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>Kaolinite 2.46</td>
<td>2.46</td>
<td>2.46</td>
<td>2.46</td>
<td>2.46</td>
<td></td>
</tr>
<tr>
<td>Illite 4.22</td>
<td>4.22</td>
<td>4.22</td>
<td>4.22</td>
<td>4.22</td>
<td></td>
</tr>
<tr>
<td>Sodium Montmorillonite 0.35</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>Total (g) 20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

The difference between the three tests is principally the mixing configuration or the position of each substance in a sample. This methodology therefore studied the interaction among oil, water and solids (clay and sand) when they are layered differently, in order to determine if the configuration of the components would have any effect on the subsequent NMR interpretations. Table 5.2 shows the different mixing configurations used for each test.

Initially in each test, the two substances that were placed in the bottom and the center of a sample were measured at 0 and 24 hours. The NMR measurements were performed at these two different times in order to verify the stability of the machine through the consistency in the results. After 24 hours, the third substance was added to the top of the sample, and the new mixture was once again measured at 0 and 24 hours. The final
distribution of fluids was governed by gravity since the samples were not shaken. Settling characteristics for agitated samples are the topic of the next stage of tailings characterization, in Chapter 6. The pulse parameters used to analyze each mixture were selected according to the type of substances mixed. For example, in Test No.1 the initial bitumen and solids (clays and sand) mixture was measured only with the pulse parameters to detect the oil signal at 0 and 24 hours. When water was added to these samples, the pulse parameters to detect both water and oil signals separately were then used to perform the measurements. The results obtained for each test are presented in the following section. All the NMR spectra shown in the figures of this chapter correspond to the mixture prepared with brine and Athabasca bitumen, since this was the system with the most similar characteristics to real tailings samples.

Table 5.2 Mixing Configurations Used in Synthetic Samples

<table>
<thead>
<tr>
<th>Position of Each Substance in a Vial</th>
<th>Test No. 1</th>
<th>Test No. 2</th>
<th>Test No. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom</td>
<td>Clays and sand</td>
<td>Clay and sand</td>
<td>Bitumen</td>
</tr>
<tr>
<td>Center</td>
<td>Bitumen</td>
<td>Water</td>
<td>Water</td>
</tr>
<tr>
<td>Top</td>
<td>Water</td>
<td>Bitumen</td>
<td>Clay and sand</td>
</tr>
</tbody>
</table>

5.2.1 Test One Results

The NMR spectrum obtained at 0 and 24 hours for the initial mixtures of Athabasca bitumen (O) and solids (S) were made using the parameters to detect the oil signal. These spectra showed a well-defined bitumen peak before 1 ms for the samples containing 3, 4 and 5 wt % of bitumen. Figure 5.1 shows the spectra obtained for the sample with 4 wt % of bitumen at both times.
The NMR tool did not detect the oil signal from the samples containing 0.2 g (1 wt %), and 0.4 g (2 wt %) of bitumen, which is a reflection of the minimum bitumen mass that can be detected in the NMR tool. This is similar to the results obtained previously in Chapter 4, for samples of oil alone or mixtures of oil and water. The average absolute error in the bitumen mass predictions for the samples containing 3 to 5 wt % of bitumen was ± 0.15 g. Moreover, it is noticeable that when the samples only contained bitumen and solids, the presence of the solids did not lead to any additional amplitude. This was expected since solids by themselves do not provide any kind of signal, and the oil is so viscous that there is no effect of surface relaxation on the oil peak location.

Figure 5.1 NMR Spectra of 4 wt % of Athabasca Bitumen and Solids Mixture at 0 and 24 hours, Oil Signal

In figure 5.2 it can be observed that when brine (W) was added to the solids and bitumen mixture, additional signal was measured from water relaxing in the pores of the clay / sand mixture. The spectra obtained for samples containing 4 and 5 wt % of bitumen, using the parameters to detect oil signal, still showed well defined bitumen peaks after 24 hours; in contrast, the sample containing 3 wt % of bitumen did not show any oil peak. The average absolute error in oil mass predictions for the samples containing 4 and 5 wt
% of bitumen was ± 0.25 g. The cut off used to determine the bitumen content in all samples was determined based on the end point of the first peak found before or around 1 ms. Again, this was similar to synthetic samples containing oil and water that were measured in Chapter 4. It was important to use the floating cut off (around 1 ms) to avoid attributing the amplitude from the water bound to clays into the bitumen amplitude. If no signal was observed until after 1 ms, then it was determined that the sample did not contain bitumen in sufficient measurable quantities, and only clay bound water had been measured.

Figure 5.2 NMR Spectra of Solids, 4 wt % of Athabasca Bitumen and Brine Mixture at 0 and 24 hours, Oil Signal

The NMR spectra illustrated in figure 5.3 corresponds to the same mixture containing 4 wt % of Athabasca bitumen, but measured using parameters to detect the water signal. In the presence of sand and clay, no fixed water cut off was used because some of the water is relaxing through surface relaxation with the solids, and these did not relax at the same time for all samples. In these NMR spectra the peaks observed before or around 100 ms correspond to clay bound water or surface relaxation effect (Coates et al., 1999). As observed previously in Chapter 4, illite and kaolinite lead to water relaxation times in the
range of 10 – 100 ms. Montmorillonite may lead to significantly faster water $T_2$ values, but for the low levels present in these synthetic tailings, the effect of the enhanced water relaxation times appears to be negligible. The peak found after 1000 ms was denominated bulk or free water. It was assumed that using parameters to detect the water signal, the signal from the oil was negligible, so all the measured amplitude was converted to the water mass. The average absolute error in water mass predictions for all the samples containing brine was ± 0.27 g.

Figure 5.3 NMR Spectra of Solids, 4 wt % of Athabasca Bitumen and Brine Mixture at 0 and 24 hours, Water Signal

Tables 5.3 and 5.4 show the bitumen and water amplitude values obtained for all the different mixtures at different times, using both pulse parameters. From these tables, it is possible to observe that the water amplitude values acquired at different times were in the same range; the maximum difference between them is 0.08 amplitude units. This indicates that for measurements of water, the NMR was performing in a stable fashion. In the case of the amplitude values for the bitumen peaks, the results at 0 and 24 hours appear to contain relatively more scatter. When the actual amplitude units are considered, however, it becomes apparent that the variations between repeat measurements are in the
same order of magnitude for the bitumen signal as well. The difference appears to be more significant simply because bitumen has a lower amplitude index than water, and also because the oil content is much lower in these synthetic tailings samples. For both fluids, the variation in amplitude between successive measurements could be attributed to external factors that affected the NMR tool, such as environment temperature; all tests in this thesis were conducted at room temperature, but it was observed that the variation in the room temperature affects the response of the NMR tool. In addition, a more noisy signal present at 0 hours also could contribute to variations between measurements.

**Table 5.3 Bitumen Peak Amplitude Values Obtained in Test One**

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>Athabasca Bitumen Content</th>
<th>Bitumen Peak Amplitude Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 %</td>
<td>2 %</td>
</tr>
<tr>
<td>S + O at 0 h</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S + O at 24 h</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S + O + W at 0 h</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S + O + W at 24 h</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table 5.4 Water Peak Amplitude Values Obtained in Test One**

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>Athabasca Bitumen Content</th>
<th>Water Peak Amplitude Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 %</td>
<td>2 %</td>
</tr>
<tr>
<td>S + O + W at 0 h</td>
<td>1.777</td>
<td>1.717</td>
</tr>
<tr>
<td>S + O + W at 24 h</td>
<td>1.787</td>
<td>1.795</td>
</tr>
</tbody>
</table>

The samples prepared with Cold Lake bitumen and distilled water yielded similar results compared to the set of samples already described. However, for these tailings the oil signal was still detected in the samples containing 3 wt % of oil. This fact could be attributed to the Cold Lake bitumen being less viscous than Athabasca bitumen; therefore, its protons possess a little more movement, which makes detection easier for the NMR tool. The average absolute errors for oil and water mass predictions in these samples were ± 0.20 g and ± 0.50 g respectively.
5.2.2 Test Two Results

The samples prepared in the Test two group contained a water layer between the bitumen and the solids, which Takamura (1982) proposed as the structure that allows for the separation of oil from the sand, or the water wetting nature of the sand.

In the first part of the Test two, solids and water were mixed and measured using the parameters to detect water signal at 0 and 24 hours. The NMR spectra and the total amplitude values obtained at both times were found to be very similar. Figure 5.4 shows the results obtained for the sample that subsequently would have 3 % wt (0.6 g) of Athabasca oil. The total amplitude obtained in this figure was due to the signal coming only from water. As in test one, the peaks observed between 10 and before 1000 ms correspond to the clays bound with water and after 1000 ms the peak represents free water. The peaks are measured at similar T\textsubscript{2} values at both 0 and 24 hours, indicating that for this solid, water immediately entered reached its equilibrium distribution between the grains of the solids. Although the amplitude at 24 hours appears to be lower than at 0 hours, if the actual amplitude values are summed the total water amplitude is similar at both times.

After 24 hours, bitumen was added and the samples were measured again with both pulse parameters at 0 and 24 hours. The behaviour of this mixture is illustrated in figures 5.5 and 5.6 using parameters to detect oil and water signal, respectively. As in Test one, the samples with 4 and 5 wt % of bitumen showed a bitumen peak close to 1 ms at 0 and 24 hours.

For the samples with 1 and 2 wt % of oil, the first peaks measured occurred close to 10 ms, which cannot be interpreted as bitumen because its relaxation time is too slow. In all cases, only the first peak (around 1 ms) was used to calculate the oil mass, and as was also the case in the Test one, bitumen below 3 wt % could not always be measured. The average absolute error in bitumen mass prediction for the samples containing 3 to 5 wt % of bitumen was ± 0.15 g. In figure 5.5 it was also possible to observe the presence of
water signal at around 10 ms, which indicates that the parameters to detect oil signal could also be used to identify fast relaxing clay-bound water. In this study, however, the water quantification was only calculated from the spectra obtained using the parameters to detect the water signal. With these parameters, the small bitumen signal was not detectable so all the amplitude was attributed to water. The average absolute error in water mass predictions was ± 0.30 g for the samples containing brine. In the case of the samples containing Cold Lake bitumen and distilled water, the average absolute errors for oil and water mass predictions were ± 0.15 g and ± 0.50 g respectively.

**Figure 5.4 NMR Spectra of Solids and Brine Mixture at 0 and 24 hours, Water Signal**

Tables 5.5 and 5.6 provide the water and bitumen peaks amplitude values for the samples of Test two. Based on these results, the amplitude values obtained for the water peaks can be considered constant, since the maximum variation in repeat measurements were 0.08 amplitude units for the solids/water mixture, and 0.06 for the solids/water/bitumen. In the case of bitumen, the amplitudes variations were in the same range and were more constant than those obtained in Test one.
Figure 5.5 NMR Spectra of Solids, Brine and 3 wt % of Athabasca Bitumen at 0 and 24 hours, Oil Signal

Figure 5.6 NMR Spectra of Solids, Brine and 3 wt % of Athabasca Bitumen at 0 and 24 hours, Water Signal

Table 5.5 Water Peak Amplitude Values Obtained in Test Two

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>Water Peak Amplitude Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Athabasca Bitumen Content</td>
<td>1 %</td>
</tr>
<tr>
<td>S + W at 0 h</td>
<td>1.778</td>
</tr>
<tr>
<td>S + W at 24 h</td>
<td>1.761</td>
</tr>
<tr>
<td>S + W + O at 0 h</td>
<td>1.762</td>
</tr>
<tr>
<td>S + W + O at 24 h</td>
<td>1.814</td>
</tr>
</tbody>
</table>

Table 5.6 Bitumen Peak Amplitude Values Obtained in Test Two

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>Bitumen Peak Amplitude Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Athabasca Bitumen Content</td>
<td>1 %</td>
</tr>
<tr>
<td>S + W + O at 0 h</td>
<td>0</td>
</tr>
<tr>
<td>S + W + O at 24 h</td>
<td>0</td>
</tr>
</tbody>
</table>
5.2.3 Test Three Results

For this test, the initial mixtures were composed of bitumen and water and were measured using both pulse parameters to detect water and oil signal at 0 and 24 hours. Well-defined bitumen peaks at around 1 ms were observed for the samples containing upwards of 3 wt % (0.6 g) of bitumen. Figures 5.7 and 5.8 show the NMR spectra for 3 wt % of Athabasca bitumen and brine mixture at 0 and 24 hours, using the parameters to detect the oil and water signal correspondingly. As was also observed previously, the oil relaxed close to 1 ms and no oil peak was observed at early relaxation times using the parameters to detect the water signal (Figure 5.8).

After 24 hours, the mixture of clays and sand was added to the samples and settled through the oil and water. The spectra obtained at different times, using the parameters to detect the oil signal, are shown in the figure 5.9 for the sample containing 3 wt % of Athabasca bitumen. An oil peak was observed only in the spectra obtained after 24
hours; the peak obtained close to 10 ms at 0 hours cannot be assumed to be oil because its relaxation time was too slow. The spectra obtained using the parameters to detect the water signal are illustrated in figure 5.10, which clearly show the presence of clays at around 100 ms. In this mixing configuration, the clays were now settling through the aqueous phase and the final settled water distribution is no longer instantaneous. Rather, the water relaxes faster after 24 hours, at which time the solids had settled and the final pore size distribution had been obtained. The average absolute errors found for bitumen and water mass predictions were ± 0.35 g and ± 0.38 g respectively.

In the samples prepared with Cold Lake oil and distilled water, oil peaks were detected only for the samples containing 4 or 5 wt % of oil. The average absolute errors for oil and water mass predictions were found to be ± 0.10 g and ± 0.6 g.

The amplitude data for the water and bitumen peaks acquired in the Test three are shown in tables 5.7 and 5.8 correspondingly. The maximum amplitude variation obtained for the water peaks in the water/oil mixtures was 0.03, and variations of 0.04 amplitude units
were measured for the water/oil/solids mixtures. The amplitude values for the bitumen peaks were very stable for the water/oil mixtures at 0 and 24 hours, but when solids were added to the mixture the oil amplitude values changed. This could be due to difficulties in discriminating the oil signal with the addition of fast relaxing bound water. When the mixtures contained only bulk water and viscous bitumen, any fast relaxing signal could be measured and its $T_2$ value identified. In contrast, when there was also a surface water signal that was changing with time, it was more difficult for both the actual acquisition and later the inversion software to discriminate between the oil and bound water peaks. Despite these additional uncertainties, the oil amplitudes still vary within the same range as the water amplitude values. As in the other sample configurations, however, the small amounts of oil coupled with the lower oil amplitude index will lead to greater errors in the predicted oil fractions.

**Table 5.7 Water Peak Amplitude Values Obtained in Test Three**

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>Water Peak Amplitude Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Athabasca Bitumen Content</td>
<td>1 %</td>
</tr>
<tr>
<td>W + O at 0 h</td>
<td>1.708</td>
</tr>
<tr>
<td>W + O at 24 h</td>
<td>1.697</td>
</tr>
<tr>
<td>W + O + S at 0 h</td>
<td>1.787</td>
</tr>
<tr>
<td>W + O + S at 24 h</td>
<td>1.826</td>
</tr>
</tbody>
</table>

**Table 5.8 Bitumen Peak Amplitude Values Obtained in Test Three**

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>Bitumen Peak Amplitude Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Athabasca Bitumen Content</td>
<td>1 %</td>
</tr>
<tr>
<td>W + O at 0 h</td>
<td>0</td>
</tr>
<tr>
<td>W + O at 24 h</td>
<td>0</td>
</tr>
<tr>
<td>W + O + S at 0 h</td>
<td>0</td>
</tr>
<tr>
<td>W + O + S at 24 h</td>
<td>0</td>
</tr>
</tbody>
</table>
5.2.4 Comparison of the Three Tests Using Different Quality of Water and Bitumen

The NMR spectra of the three tests using different qualities of oil and water showed similar behaviour to one another. This can be observed in figures 5.11 and 5.12, which present the NMR spectra obtained to measure the samples containing 3 wt % of bitumen, water and solids using the parameters to detect the oil signal.

As discussed above, the Cold Lake bitumen tended to relax slower than Athabasca bitumen. This phenomenon is attributed to differences in viscosity, which made it possible to detect more oil signal and consequently for the oil to have higher amplitude values in all three tests. Correspondingly, in Chapter 4 it was observed that the Cold Lake oil amplitude index was higher than that of Athabasca bitumen.

Table 5.9 presents the final amplitude values of the Cold Lake and Athabasca bitumen peaks for all three tests. These results show that NMR tool could not detect 1 or 2 wt % of bitumen in any of the samples, and in some cases even 3 wt % could not be detected. The final conclusion from this data is that when measuring small amounts of viscous bitumen, the NMR tool is able to detect oil in samples that contain amounts higher than 0.6 g of oil. This detection limit will be different for different NMR machines, and will be affected by low levels of noise in the measurements. As a result, fine-tuning and calibration for each specific machine used is very important for measurements of low oil content in tailings samples.

Table 5.9 Final Amplitude Values of the Cold Lake and Athabasca Bitumen Peaks for the Three Tests

<table>
<thead>
<tr>
<th>Bitumen Content</th>
<th>1 %</th>
<th>2 %</th>
<th>3 %</th>
<th>4 %</th>
<th>5 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of Bitumen</td>
<td>CL</td>
<td>A</td>
<td>CL</td>
<td>A</td>
<td>CL</td>
</tr>
<tr>
<td>Test 1</td>
<td>0.100</td>
<td>0.032</td>
<td>0.126</td>
<td>0.049</td>
<td></td>
</tr>
<tr>
<td>Test 2</td>
<td>0.103</td>
<td>0.026</td>
<td>0.112</td>
<td>0.062</td>
<td>0.123</td>
</tr>
<tr>
<td>Test 3</td>
<td>0.129</td>
<td>0.018</td>
<td>0.106</td>
<td>0.025</td>
<td>0.115</td>
</tr>
</tbody>
</table>

CL: Cold Lake bitumen   A: Athabasca bitumen
The other observation that can be made from Table 5.9 is that, in general, there is less variation in the oil amplitude units between Tests 1 to 3 for Cold Lake oil, compared to Athabasca bitumen. Again, lower viscosity oils yield more measurable amplitude, which makes the subsequent generation of the spectra more stable. The direct implication of this result is that if Athabasca bitumen were measured at slightly higher temperatures in the plant, the oil viscosity would correspondingly be lower and the NMR measurements would become proportionally more stable.

Interestingly, when the actual errors in the oil mass predictions are compared for Cold Lake and Athabasca bitumen (Sections 5.2.1 to 5.2.3), the errors are not smaller for the Cold Lake oil, despite its lower viscosity. This leads to another conclusion for the oil measurements: although lower viscosity oil may yield more stable spectra under different mixing configurations, when small amounts of high viscosity bitumen are present, it is still difficult to accurately quantify the bitumen content.
The NMR spectra obtained using the pulse parameters to detect the water signal showed a similar behaviour for the two types of water (figures 5.13 and 5.14). Both water qualities show bulk water peaks above 1000 ms, and clay-bound water signals around 10 – 100 ms. However, the samples prepared with distilled water presented more water relaxing at times below 1000 ms, and proportionally lower bulk water amplitudes for the same water and solids masses. This was deduced by comparing the relative size and amplitude of the free waters peaks in figures 5.13 and 5.14. The reason for this difference is likely due to increased clay swelling in the distilled water samples. Ions in the aqueous phase tend to collapse the clay and lead to the creation of more free water; under distilled water conditions the clays are more swollen and thus a higher water amplitude fraction is associated with surface relaxation. The final amplitude values of the distilled water and brine peaks are showed for all the three tests in table 5.10, which in general were in the same range as one another.

Figure 5.13 NMR Spectra of 3 wt % of Athabasca Bitumen, Brine and Solids Mixture, Water Signal

Figure 5.14 NMR Spectra of 3 wt % of Cold Lake Bitumen, Distilled Water and Solids Mixture, Water Signal
The results obtained from NMR measurements on these synthetic tailings samples allow for several main findings to be summarized. Accuracy of oil content predictions was strongly dependent on proper acquisition of the oil signal (i.e. a “clean” measured signal) and a proper oil amplitude index. The NMR tool was able to detect bitumen in amounts higher than 0.6 g, with a maximum average error of 0.35 g. Water could be detected in all samples with a maximum average error of 0.60 g; although this number appears to be higher than the error in the oil content, there is significantly more water present in tailings so the errors are much lower for the water. Finally, NMR measurements in general provide the same level of accuracy for tailings samples in all three configurations tested. Therefore, the methods of spectrum analysis developed in this study can be applied in predictions of actual real tailings samples, which will have been mixed in unknown configurations of fluids and solids.

Table 5.10 Final Amplitude Values of the Distilled Water and Brine Peaks for the Three Tests

<table>
<thead>
<tr>
<th>Bitumen Content</th>
<th>Type of Water</th>
<th>Amplitude Values for Water Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DW</td>
<td>B</td>
</tr>
<tr>
<td>1 %</td>
<td>2 %</td>
<td>3 %</td>
</tr>
<tr>
<td>4 %</td>
<td>5 %</td>
<td></td>
</tr>
<tr>
<td>Test 1</td>
<td>1.441</td>
<td>1.787</td>
</tr>
<tr>
<td></td>
<td>1.961</td>
<td>1.795</td>
</tr>
<tr>
<td></td>
<td>1.758</td>
<td>1.756</td>
</tr>
<tr>
<td></td>
<td>1.507</td>
<td>1.714</td>
</tr>
<tr>
<td></td>
<td>1.776</td>
<td>1.657</td>
</tr>
<tr>
<td>Test 2</td>
<td>1.793</td>
<td>1.814</td>
</tr>
<tr>
<td></td>
<td>1.730</td>
<td>1.740</td>
</tr>
<tr>
<td></td>
<td>1.756</td>
<td>1.733</td>
</tr>
<tr>
<td></td>
<td>1.776</td>
<td>1.688</td>
</tr>
<tr>
<td></td>
<td>1.633</td>
<td>1.650</td>
</tr>
<tr>
<td>Test 3</td>
<td>2.067</td>
<td>1.826</td>
</tr>
<tr>
<td></td>
<td>1.556</td>
<td>1.756</td>
</tr>
<tr>
<td></td>
<td>1.784</td>
<td>1.701</td>
</tr>
<tr>
<td></td>
<td>1.670</td>
<td>1.702</td>
</tr>
<tr>
<td></td>
<td>1.825</td>
<td>1.641</td>
</tr>
</tbody>
</table>

DW: distilled water     B: brine

5.3 Analysis of Real Tailings Samples

Shell Canada Research Center, located in Calgary, Alberta, provided a total of 34 blind tailings samples that had been prepared from tests performed in a batch extraction unit (BEU). These samples were divided in two main groups, constituted by 22 and 12 samples, respectively. These samples were initially measured twice in the NMR tool using the new method; subsequently, the oil, water and solids content of the same samples were determined by the Dean Stark method. This methodology was designed to
test the NMR predictions in blind samples against those obtained by the Dean Stark extraction method, which is the accepted method used in the industry to characterize tailings samples. Additionally, Shell Canada prepared sister samples of the first and second group of blind samples and sent them also for Dean-Stark analysis. The goal of the testing with sister samples was to evaluate if they possessed the same compositional characteristics as the other blind samples. If so, then wider testing could eventually be done at the plant scale, by sending sister samples for NMR analysis while process modifications were made based on the original tailings.

5.4 Overview of Dean Stark Extraction Process

The Dean Stark (DS) extraction process is a method through which it is possible to measure fluid saturations in a sample by distillation. Fundamentally, the water in the sample is vaporized by boiling solvent (toluene), and then is condensed and collected in a calibrated trap. This allows for direct measurement of the volume of water in the sample. The solvent is also condensed, and then flows back over the sample to extract the oil. Extraction continues for approximately 24 hours.

The sample weight is measured before and after extraction. The solids content is also measured directly after drying the solids in an oven. With the initial weight and measured amounts of solids and water, the oil content could theoretically be determined by difference. However, the methodology employed by Shell Canada is one of “full reflux”, whereby the oil content is also measured directly in order to evaluate the closure of the mass balance. In this technique, the oil content is determined by the filter paper method that consists of applying an aliquot of the solvent/bitumen liquid mixture onto a piece of filter paper in a circulating manner, starting from the centre of the filter paper and moving outwards. First, the oil-toluene mixture is filled to a known total volume, and then a known aliquot of solution is sub-sampled and poured onto the filter paper. The initial weight of the filter paper is measured, as is the weight of the paper and oil after solvent has been allowed to evaporate. The bitumen fraction is taken as the measured bitumen mass from the aliquot, normalized to the volume of the total oil-solvent mixture. Figures
5.15 and 5.16 illustrate a Dean Stark apparatus in use and a filter paper with bitumen used by the Shell team in the characterization of the tailings samples.

Although Dean-Stark is the industry-accepted method for measuring the oil, water and solids content, it should be emphasized that, like any measurement, there are errors associated with this technique. The errors in the Shell Canada process are confidential, however published sources (ASTM, 2005) state that the repeatability of the Dean Stark method will be ± 0.1 ml of water or 2% of the mean water content, whichever is greater. This refers to tests that are performed by the same operator using the same apparatus, on identical material and under the same conditions. For the real middlings and tailings measured in this study, this gives errors in the water content between 0.1 – 0.3 mL of water. In tailings samples, when the oil content is on the order of less than 0.5 g of bitumen, an error in the water content can possibly be translated to the oil.

Figure 5.15 A Dean Stark Apparatus in Use in the Shell Canada Research Centre

Figure 5.16 Filter Paper with Bitumen Applied in Circulated Manner
5.5 First Group of Real Tailings Samples

The first group of real tailings samples was subdivided in two smaller groups by the Shell team. None of information about the samples was initially provided, in order to evaluate the predictions coming from the NMR technique using the bimodal compositional detection method on these blind samples. The two subgroups were composed of vials 1 to 10 and 11 to 22, respectively. The weight range of the two subgroups was 44 - 51 g and 22 - 33 g, in that order. The errors are presented as both mass units and percentages of the total sample mass.

5.5.1 Analysis of the First Group of Real Tailings Samples Using Parameters to Detect Water Signal

The samples were initially measured using the pulse parameters to detect the water signal; as a result the average water content for samples 1 to 10 was found to be 7.88 g (17.1 wt %), compared to 20.19 g (69 wt %) for samples 11 to 22. Assuming a low oil content present in the tailings, this yields a solids content on the order of 80 wt % in the first ten samples, and 30 wt % in the second group of twelve samples. Based on these results, it was inferred that the first set of samples was representative of the tailings (i.e. the bottom) stream from separation processes, which should contain a higher weight fraction of solids. These solids will also contain a proportionally higher fraction of coarse sand, compared to middlings. Samples 11 to 22, conversely, are more representative of middlings. These samples were inferred to contain less solids, but these solids would likely consist mainly of clay suspensions. These assumptions were later confirmed when the NMR results were compared with the results obtained by Shell using the Dean Stark extraction method, and through identification of the water peak locations in the measured samples.

Tables 5.11 and 5.12 present the results obtained using both techniques, and the absolute error found for each one of the samples. The average absolute errors in water content for samples 1 to 10 (tailings) and 11 to 22 (middlings) were found to be 0.36 g and 0.42 g, in
that order. These results show that the NMR technique can be considered as a potential tool in the prediction of the water content in middlings and tailings in the oil sands extraction process. The graphical comparison of the NMR and DS results acquired for tailings and middlings samples are also illustrated in figures 5.17 and 5.18 correspondingly.

Table 5.11 NMR and Dean Stark (DS) Water Content Results of Samples 1 to 10 (Tailings)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR Water Content (g)</td>
<td>6.32</td>
<td>6.20</td>
<td>7.37</td>
<td>8.22</td>
<td>8.70</td>
<td>6.99</td>
<td>8.13</td>
<td>8.53</td>
<td>8.06</td>
<td>10.36</td>
</tr>
<tr>
<td>DS water content (g)</td>
<td>6.53</td>
<td>6.11</td>
<td>7.03</td>
<td>7.99</td>
<td>8.66</td>
<td>7.07</td>
<td>7.64</td>
<td>7.65</td>
<td>7.6</td>
<td>9.57</td>
</tr>
<tr>
<td>Absolute Error (g)</td>
<td>0.21</td>
<td>0.09</td>
<td>0.34</td>
<td>0.23</td>
<td>0.04</td>
<td>0.08</td>
<td>0.49</td>
<td>0.88</td>
<td>0.46</td>
<td>0.79</td>
</tr>
<tr>
<td>Percentage Error</td>
<td>0.41</td>
<td>0.18</td>
<td>0.72</td>
<td>0.53</td>
<td>0.09</td>
<td>0.16</td>
<td>1.08</td>
<td>2.00</td>
<td>1.05</td>
<td>1.71</td>
</tr>
</tbody>
</table>

Table 5.12 NMR and Dean Stark (DS) Water Content Results of Samples 11 to 22 (Middlings)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR Water Content (g)</td>
<td>18.51</td>
<td>16.59</td>
<td>17.40</td>
<td>21.48</td>
<td>19.83</td>
<td>22.39</td>
</tr>
<tr>
<td>DS Water Content (g)</td>
<td>18.39</td>
<td>16.18</td>
<td>16.67</td>
<td>21.43</td>
<td>19.42</td>
<td>22.48</td>
</tr>
<tr>
<td>Absolute Error (g)</td>
<td>0.12</td>
<td>0.41</td>
<td>0.73</td>
<td>0.05</td>
<td>0.41</td>
<td>0.09</td>
</tr>
<tr>
<td>Percentage Error</td>
<td>0.43</td>
<td>1.34</td>
<td>2.49</td>
<td>0.20</td>
<td>1.60</td>
<td>0.34</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>17</th>
<th>18</th>
<th>19</th>
<th>20</th>
<th>21</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR Water Content (g)</td>
<td>20.63</td>
<td>16.82</td>
<td>17.10</td>
<td>20.19</td>
<td>20.30</td>
<td>22.05</td>
</tr>
<tr>
<td>DS Water Content (g)</td>
<td>20.91</td>
<td>16.28</td>
<td>16.33</td>
<td>21.01</td>
<td>20.25</td>
<td>22.8</td>
</tr>
</tbody>
</table>
Absolute Error (g) | 0.09 | 0.28 | 0.54 | 0.77 | 0.82 | 0.05
---|---|---|---|---|---|---
Percentage Error | 0.98 | 1.68 | 2.37 | 2.98 | 0.19 | 2.79

Figure 5.17 Comparison of Water Content Results of Samples 1 to 10 (Tailings) Using NMR and DS Techniques

Figure 5.18 Comparison of Water Content Results of Samples 11 to 22 (Middlings) Using NMR and DS Techniques
5.5.2 Analysis of the First Group of Real Tailings Samples Using Parameters to Detect Oil Signal

Samples 1 to 22 were also measured in the NMR tool using the pulse parameters to detect the oil signal. In the samples 1 to 10, oil was detected only in 4 samples; however, the amounts predicted were under 0.60 g, which through the synthetic samples had been established as the minimum detection limit for this machine. Based on this fact and taking into account that the results obtained from the water signal indicated that samples 1 to 10 were tailings, which usually contain very little oil, it was presumed that the measured signal at very early relaxation times would be strongly affected by small amounts of noise present during the early echoes. As a result, it was not possible to identify how much of the measured amplitude was actually related to bitumen, and how much was noise. Thus, the predicted oil masses were not expected to be accurate.

In the case of samples 11 to 22, oil was detected in 9 out of 12 samples but as in the other subgroup, the amounts predicted were still under 0.60 g. Once again, therefore, these samples should have been below the detection limit for this machine. However, based on the results obtained from the water signal, these samples were assumed to be middlings, which typically have a higher amount of oil in comparison to tailings. This led to two possibilities: either the value of detection limit was actually lower than what was measured for the synthetic samples, or the signal obtained from the measurements was once again a combination of the amplitude of the bitumen and noise. Afterwards, the NMR results were compared with those obtained by Dean Stark method and it was found that in most of the cases bitumen content in the samples were over predicted by the NMR technique. Therefore, it was concluded that the measured amplitude values at early relaxation times (around 1 ms) were strongly affected by noise in the measurements, and the NMR predictions of oil mass will not be accurate even with optimized acquisition parameters. Tables 5.13 and 5.14 show the average absolute errors found between Dean Stark and NMR for all samples. In addition, figures 5.19 and 5.20 illustrate the differences resulting from both measurements.
Table 5.13 NMR and Dean Stark (DS) Bitumen Content Results of Samples 1 to 10 (Tailings)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR Bitumen content (g)</td>
<td>0.00</td>
<td>0.18</td>
<td>0.00</td>
<td>0.37</td>
<td>0.00</td>
<td>0.00</td>
<td>0.50</td>
<td>0.00</td>
<td>0.00</td>
<td>0.37</td>
</tr>
<tr>
<td>DS Bitumen Content (g)</td>
<td>0.07</td>
<td>0.23</td>
<td>0.02</td>
<td>0.20</td>
<td>0.07</td>
<td>0.15</td>
<td>0.13</td>
<td>0.08</td>
<td>0.02</td>
<td>0.10</td>
</tr>
<tr>
<td>Absolute Error (g)</td>
<td>0.07</td>
<td>0.06</td>
<td>0.02</td>
<td>0.17</td>
<td>0.07</td>
<td>0.15</td>
<td>0.36</td>
<td>0.08</td>
<td>0.02</td>
<td>0.27</td>
</tr>
<tr>
<td>Percentage Error</td>
<td>0.001</td>
<td>0.001</td>
<td>0.0004</td>
<td>0.004</td>
<td>0.02</td>
<td>0.003</td>
<td>0.008</td>
<td>0.002</td>
<td>0.0004</td>
<td>0.006</td>
</tr>
</tbody>
</table>

Table 5.14 NMR and Dean Stark (DS) Bitumen Content Results of Samples 11 to 22 (Middlings)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR Bitumen Content (g)</td>
<td>0.26</td>
<td>0.16</td>
<td>0.39</td>
<td>0.00</td>
<td>0.26</td>
<td>0.00</td>
</tr>
<tr>
<td>DS Bitumen Content (g)</td>
<td>0.20</td>
<td>0.03</td>
<td>0.30</td>
<td>0.25</td>
<td>0.17</td>
<td>0.03</td>
</tr>
<tr>
<td>Absolute Error (g)</td>
<td>0.06</td>
<td>0.13</td>
<td>0.09</td>
<td>0.25</td>
<td>0.09</td>
<td>0.03</td>
</tr>
<tr>
<td>Percentage Error</td>
<td>0.21</td>
<td>0.43</td>
<td>0.30</td>
<td>1.07</td>
<td>0.37</td>
<td>0.12</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>17</th>
<th>18</th>
<th>19</th>
<th>20</th>
<th>21</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR Bitumen Content (g)</td>
<td>0.18</td>
<td>0.29</td>
<td>0.26</td>
<td>0.01</td>
<td>0.37</td>
<td>0.00</td>
</tr>
<tr>
<td>DS Bitumen Content (g)</td>
<td>0.28</td>
<td>0.13</td>
<td>0.08</td>
<td>0.18</td>
<td>0.30</td>
<td>0.12</td>
</tr>
<tr>
<td>Absolute Error (g)</td>
<td>0.11</td>
<td>0.16</td>
<td>0.18</td>
<td>0.17</td>
<td>0.07</td>
<td>0.12</td>
</tr>
<tr>
<td>Percentage Error</td>
<td>0.38</td>
<td>0.49</td>
<td>0.55</td>
<td>0.62</td>
<td>0.25</td>
<td>0.43</td>
</tr>
</tbody>
</table>
Figure 5.19 Comparison of Bitumen Content Results of Samples 1 to 10 (Tailings) Using NMR and DS Techniques

![Graph showing comparison of bitumen content results for samples 1 to 10 using NMR and DS techniques.](image)

Figure 5.20 Comparison of Bitumen Content Results of Samples 11 to 22 (Middlings) Using NMR and DS Techniques

![Graph showing comparison of bitumen content results for samples 11 to 22 using NMR and DS techniques.](image)
Finally, table 5.15 presents the average percent content of bitumen, water and solids found for all 22 samples by means of the Dean Stark extraction method, performed by the Shell Canada Research Centre. It is significant that in the middlings, which did in fact contain more oil mass than the tailings, an apparent oil signal was measured in many of the samples. This leads to an important conclusion: the signal at early times cannot be fully discarded and assumed to be the contribution from noise alone. Even though the samples contained under 0.6 g of bitumen, the fine-tuned NMR machine was still able to discern samples with higher oil content. However, when the samples contain under 0.6 g of bitumen, the NMR measurements of bitumen amplitude cannot be accurately quantified.

### Table 5.15 Average Compositional Results of Samples 1 to 22 Using DS Method

<table>
<thead>
<tr>
<th>Description</th>
<th>Sample No.</th>
<th>% Bitumen</th>
<th>% Water</th>
<th>% Solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tailings</td>
<td>1-10</td>
<td>0.23</td>
<td>16.69</td>
<td>83.07</td>
</tr>
<tr>
<td>Middlings</td>
<td>11-22</td>
<td>0.63</td>
<td>68.83</td>
<td>30.54</td>
</tr>
</tbody>
</table>

#### 5.6 Second Group of Real Tailings Samples

After the first set of 22 real tailings samples had been analyzed, Shell Canada was encouraged by the preliminary findings and decided to provide a second set of blind samples for further analysis. This set of 12 real tailings samples was provided based on their internal identification of varying qualities of oil sands, in order to determine if bitumen contents could be identified below the detection limit obtained from the synthetic samples. The weight range of these samples was between 25 to 43 g.

All samples were again initially measured using the parameters to detect the water signal. From the NMR predictions, it was determined that the average water content for samples 1 to 6 was 4.76 g (11.7 wt %), and was 18.03 g (66.3 wt %) for samples 7 to 12. Additionally, the water peak locations in samples 1 to 6 were also at longer relaxation times than for samples 7 to 12, indicating a higher fraction of coarse solids in these
samples. From the NMR estimations of water and solids content, it was inferred that samples 1 to 6 were tailings and samples 7 to 12 were middlings.

It was then expected that more oil would once again be detected in the second set of samples, when measured using the oil parameters. However, for these samples the NMR tool was only able to detect a signal in the range of $T_2$ values associated with oil for two samples out the twelve, and the amount predicted was again under the established detection limit. Therefore, it was expected that these samples would contain less oil than the original set of samples, and that the bitumen amplitude in the two samples where signal was measured would be strongly affected by noise.

The results were compared with those obtained through the Dean Stark technique and the average absolute error in water mass predictions was found to be 0.44 g. This was similar to the range of errors seen in the previous samples, and also in synthetic sample measurements. For higher water content, this is a small relative error so the NMR is able to predict water content accurately. NMR oil mass predictions were only made for the two samples where some amplitude was detected; in the other samples the NMR predicted no bitumen. Tables 5.16 and 5.17 show the water and oil content determined for samples 1 to 12 using the NMR technique and the Dean Stark method, and the absolute error found for each one of the samples. Furthermore, table 5.18 provides the average compositional results found for samples 1 to 12 using the Dean Stark method. Finally, the graphical comparison between the two techniques is illustrated in figures 5.21 and 5.22.
### Table 5.16 NMR and Dean Stark (DS) Water Content Results of Samples 1 to 12

<table>
<thead>
<tr>
<th>Sample No. (Tailings)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR Water Content (g)</td>
<td>3.19</td>
<td>6.10</td>
<td>4.24</td>
<td>3.73</td>
<td>4.80</td>
<td>6.47</td>
</tr>
<tr>
<td>DS Water Content (g)</td>
<td>3.78</td>
<td>6.63</td>
<td>3.76</td>
<td>3.78</td>
<td>4.49</td>
<td>6.02</td>
</tr>
<tr>
<td>Absolute Error (g)</td>
<td>0.59</td>
<td>0.53</td>
<td>0.48</td>
<td>0.05</td>
<td>0.31</td>
<td>0.45</td>
</tr>
<tr>
<td>Percent Error</td>
<td>1.74</td>
<td>1.23</td>
<td>1.17</td>
<td>0.13</td>
<td>0.76</td>
<td>1.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No. (Middlings)</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR Water Content (g)</td>
<td>16.94</td>
<td>17.17</td>
<td>19.40</td>
<td>17.80</td>
<td>19.06</td>
<td>17.83</td>
</tr>
<tr>
<td>DS Water Content (g)</td>
<td>17.40</td>
<td>16.20</td>
<td>19.53</td>
<td>17.44</td>
<td>19.44</td>
<td>18.35</td>
</tr>
<tr>
<td>Absolute Error (g)</td>
<td>0.46</td>
<td>0.97</td>
<td>0.13</td>
<td>0.36</td>
<td>0.38</td>
<td>0.52</td>
</tr>
<tr>
<td>Percent Error</td>
<td>1.71</td>
<td>3.43</td>
<td>0.52</td>
<td>1.23</td>
<td>1.32</td>
<td>1.98</td>
</tr>
</tbody>
</table>

### Table 5.17 NMR and Dean Stark (DS) Oil Content Results of Samples 1 to 12

<table>
<thead>
<tr>
<th>Sample No. (Tailings)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR Bitumen Content (g)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>DS Bitumen Content (g)</td>
<td>0.10</td>
<td>0.17</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.13</td>
</tr>
<tr>
<td>Absolute Error (g)</td>
<td>0.10</td>
<td>0.17</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.13</td>
</tr>
<tr>
<td>Percent Error</td>
<td>0.29</td>
<td>0.39</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.31</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No. (Middlings)</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR Bitumen Content (g)</td>
<td>0.47</td>
<td>0.10</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>DS Bitumen Content (g)</td>
<td>0.28</td>
<td>0.25</td>
<td>0.18</td>
<td>0.22</td>
<td>0.18</td>
<td>0.03</td>
</tr>
<tr>
<td>Absolute Error (g)</td>
<td>0.18</td>
<td>0.15</td>
<td>0.18</td>
<td>0.22</td>
<td>0.18</td>
<td>0.03</td>
</tr>
<tr>
<td>Percent Error</td>
<td>0.68</td>
<td>0.54</td>
<td>0.73</td>
<td>0.77</td>
<td>0.64</td>
<td>0.13</td>
</tr>
</tbody>
</table>
Table 5.18 Average Compositional Results of Samples 1 to 12 Using DS Method

<table>
<thead>
<tr>
<th>Description</th>
<th>Sample No.</th>
<th>% Bitumen</th>
<th>% Water</th>
<th>% Solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tailings</td>
<td>1-6</td>
<td>0.19</td>
<td>11.92</td>
<td>87.89</td>
</tr>
<tr>
<td>Middlings</td>
<td>7-12</td>
<td>0.75</td>
<td>66.91</td>
<td>32.34</td>
</tr>
</tbody>
</table>

Figure 5.21 Comparison of Water Content Results of Samples 1 to 12 Using NMR and DS Techniques

Figure 5.22 Comparison of Oil Content Results of Samples 1 to 12 Using NMR and DS Techniques
As expected, these samples did in fact contain less oil mass than the original 22 samples. Once again, therefore, NMR oil measurements were able to discern that there was very little oil present. Moreover, signal was detected only in the samples containing the most oil. However, since the oil masses were consistently below the determined oil detection limit, it is apparent from table 5.17 and figure 5.22 that the oil content cannot be quantified.

In general, oil content could not be accurately quantified in the samples that contained less than 0.6 g of oil. However, the results of the NMR oil measurements are still valuable because the identification of a larger oil signal could still serve as a warning that there is too much oil present in the tailings. Moreover, it may be possible to obtain more accurate measurements of water and oil content through a combination of NMR and other measurements. One alternative could be to first measure water content using NMR and then add toluene to the sample, applying agitation to dilute the oil and separate it from the sand and water. The oil/toluene mixture could then be siphoned out, and by subtracting the mass of toluene from that of the mixture, the oil content could possibly be measured. Another alternative could be to once again measure the water content through NMR, and then to vaporize the water using microwaves. The remaining signal would all be hot bitumen, which should be easier to measure. These process alternatives could be tested in the future.

5.7 Comparison of Dean Stark Results for Sister Samples

In most tests that are carried out in order to test a new technology, an effort is made to eliminate bias in the predictions. In this spirit, comparative studies are usually performed as blind samples in different laboratories. In this case, NMR tests were first done on samples that were provided by Shell Canada, but at the same time, sister (twin) tailings/middlings were also extracted for Dean-Stark analysis. As mentioned previously, the other goal of this study was to determine if NMR measurements would be similar to the results obtained on sister samples. If this were possible, then ideally a wider testing program could be initiated in actual plant samples, whereby some samples would be
collected for NMR analysis while process modifications would be based on measurements performed on these sister samples. When the NMR predictions were compared against the sister sample Dean-Stark numbers, there was considerable scatter even in the water predictions. Therefore, the samples that had been analyzed in the NMR were later sent for Dean-Stark analysis as well. Figure 5.23 shows a comparison between the Dean Stark water masses results for the original samples vs. their sister samples. These samples belong to the first group of samples analyzed (1 to 10), which were found to be tailings. The oil mass results are also compared in figure 5.24.

Figure 5.23 Dean Stark Water Masses Results for the Original vs. Sister Samples

The difference between the original and sister samples leads to a very important observation regarding measurements of tailings samples: for such heterogeneous systems, considerable error can be introduced by comparing NMR results to sister samples. In order to evaluate NMR applications in tailings, it is imperative to compare NMR and Dean-Stark on the same samples. In plant-scale operations, the fact that middlings and tailings are so heterogeneous also means that in order to determine that a given middlings or tailings stream has a certain oil, water or solids content, multiple measurements should
be taken and averaged. A single NMR measurement may not be representative of the actual middlings or tailings composition in the plant at that time.

Figure 5.24 Dean Stark Oil Masses Results for the Original vs. Sister Samples

5.8 Interpretation of Solids Properties from NMR Water Measurements

The identification of a sample as being from the middlings or tailings stream was related to the relative fraction of water and solids, and also to the nature of the solids themselves. Unless a significant oil signal is measured, the middlings or tailings will contain very little oil. Therefore, since it is known that the NMR water content predictions are accurate, subtracting the NMR water mass from the total mass of the sample gives a first-pass estimate of the solids, and this is denominated “solids by difference”. Figures 5.25 and 5.26 show the solids mass predictions, using the NMR and DS techniques, for the two groups of real samples analyzed. As expected, the calculation of solids mass by difference is similar to the measured solids mass from Dean-Stark extraction method. The average absolute errors for the first and second groups of samples were found to be 0.50 and 0.60 g, respectively. Since the solids are determined by difference using the NMR
estimates of the water mass, the errors in the solids will be directly proportional to the errors in the water mass predictions.

Figure 5.25 Comparison of Solids Mass Predictions of Samples 1 to 22 (First group) Using NMR and DS Techniques

Figure 5.26 Comparison of Solids Mass Predictions of Samples 1 to 12 (Second Group) Using NMR and DS Techniques
As mentioned previously, by knowing the solids fraction, the type of sample (middlings or tailings) can already be identified. However, the spectra generated using the NMR water parameters can also provide an indication of the nature of the solids. Figure 5.27 and 5.28 show example NMR spectrum of a tailings and middlings sample, respectively. These spectra were acquired using the parameters to detect the water signal.

It is apparent from comparing these spectra that the middlings contain faster relaxing water peaks, compared to the tailings. This corresponds to water bound to clay; although the solids content is lower in middlings, the water is all physically constrained by the suspended clays.

The significance of this observation is that the nature of the solids (sand vs. clays) will lead to distinct differences in the settling behaviour of the tailings. Therefore, the spectra obtained using the parameters to detect the water signal do not just provide an indication of the water content and the type of sample being measured, but they also provide
information regarding the settling properties of the suspended solids. This topic will be discussed in the next chapter.

5.9 Summary

It has been demonstrated that an NMR bimodal compositional detection method may be used to estimate water and bitumen content in synthetic tailings samples. These measurements, which can be obtained in approximately fifteen minutes, were then validated against real tailings. Two qualities of water and bitumen were used to prepare the synthetic samples, and the samples were analyzed using different mixing configurations, as a function of time. Through the measurement of these samples, it was determined that the NMR tool is able to detect bitumen in amounts higher than 0.6 g. In addition, it was found that the maximum absolute errors of bitumen and water mass predictions in synthetic tailings samples with a total mass 20 g were ± 0.35 g and ± 0.60 g, respectively. These results are significant, because they show that NMR can be used to measure samples containing a small amount of oil and a large amount of fine solids. In NMR applications in tailings monitoring, this same procedure for identifying the accuracy and detection limits for oil should be performed with the machine actually being used in the plant.

A total of 34 real tailings samples were measured in the NMR tool, and the bitumen and water mass predictions were compared with the results obtained using the Dean Stark extraction method. NMR water contents were accurate when compared against Dean-Stark values, and the spectra could also be used to infer the nature of the solids in the samples (i.e. coarse sand or fine clays). With this information, the samples can be identified as being either tailings or middlings. For all of the real samples provided, the oil masses present were under the detection limit that had been determined from the synthetic tailings samples. In many samples, therefore, no oil amplitude was measured. For samples containing a higher proportion of bitumen, it was observed that some oil amplitude could be detected, but for under 0.6 g of bitumen this oil content could not be quantified.
Although higher oil masses appear to be required in order to accurately measure the bitumen content, the results obtained for the real tailings are still important. A possible application of the NMR tool that could arise out of this study is a flag or warning that the oil content in the middlings or tailings is too high. Therefore, while NMR may not be valid for analytical measurements of the oil content, the simple detection of a large oil signal can serve as a warning that the process in the plant is not operating efficiently. Measurements of water and solids content can be made at a much more analytical level.
CHAPTER 6: ANALYSIS OF TAILINGS SETTLING BEHAVIOR

6.1 Introduction

Synthetic and real tailings samples were tested to observe variations in their settling characteristics. The properties of these samples were studied through changes in the NMR spectra over time and in the values of their geometric mean relaxation times ($T_{2gm}$). Synthetic samples were initially used to evaluate the settling behaviour as a function of clay content and salinity; subsequently, real samples were used to study the effect of different concentrations of flocculant, coagulant and a mixture of both on the tailings settling rates. The chemical additives used during the analysis were of the same quality as those used in the industrial process performed by Shell Canada.

The NMR results obtained with the real tailings samples were compared against those obtained using settling columns, which is the typical method used in the industry to study tailings settling rates. The objective of these analyses was to determine if in a short time it would be possible to monitor the effectiveness of the chemical additives over the tailings settling rates. This would in turn allow for a faster recovery of a larger amount of warm water that could be reincorporated into the oil sands process.

The water and oil content of the samples were calculated through the amplitude index ($AI$) definition in the same manner as in the analyses discussed previously in Chapters 4 and 5. In measurements of settling, however, the analyses were performed based on the relative amplitude values of the free or bulk water peaks compared to surface-bound water. Settling was also studied through the values of the geometric mean relaxation time of the water signal with time, since this parameter provides information about the solid-fluid interaction in a sample.

Overall, the results obtained showed that the NMR technique has potential to be used as an on-site fast tool in the management of tailings, since the spectra generated by this technique can be used to differentiate the effect of flocculant, gypsum or both on the
tailings settling rates. NMR spectra can also establish if it is necessary to add a larger proportion of these substances to improve water release (Motta et al., 2008a, 2008b)

6.2 Settling Behaviour Analysis of Tailings Synthetic Samples

Synthetic samples were used initially to analyze the settling behaviour as a function of clay content and salinity. Two sets of synthetic samples, with a total mass 20 g per sample, were prepared and each set consisted of three samples (high, medium and low fines content in the solids). Each synthetic tailings sample contained 1.5 wt % of bitumen, 62 wt % of water and 36.5 wt % of solids. Two types of bitumen and water were used to determine if their properties would affect the settling behavior of tailings. As in the previous studies, Cold Lake bitumen and distilled water were used in the preparation of the first set, to investigate the response of a low salinity aqueous phase and a lower viscosity oil. Athabasca bitumen and brine were used in the preparation of the second set of mixtures.

The solids content (36.5 wt %) was distributed among the three samples in each set as 100 wt %, 50 wt % and 5 wt % of sand, with the remaining percentage consisting of a mixture of the typical clays composition found in fine tailings: 60 wt % of illite, 35 wt % of kaolinite and 5 wt % of sodium montmorillonite. The samples were prepared with a water layer between the solids and oil layers.

All the samples were measured in the NMR tool at zero hours, which was considered to be the stability state because they had not been previously agitated, so the solids were already settled. Subsequently, the samples were again measured at 3, 6 and 24 hours to verify the stability of the spectra with time. Both sets of samples were then shaken for 20 minutes and measured immediately afterwards. These samples were also measured at 3, 6 and 24 hours after agitation. A Burrell wrist action shaker was used to agitate the samples and suspend the solids into the oil and water. All mixtures were measured again in the NMR tool after one week, two months and three months to analyze natural gravity sedimentation. The effects of evaporation were taken in account in the water mass predictions in all the samples.
6.2.1 Results of Settling Behaviour of Synthetic Samples

The spectra obtained at different times for all synthetic samples were acquired using the pulse parameters to detect the water signal, since solids settling is governed by slower relaxing signals (> 10 ms up to bulk relaxation values > 1000 ms). No significant change in the amplitude values was observed at 3 and 6 hours; therefore, in the spectra presented these values have been omitted to simplify the plots.

Figure 6.1 illustrates the settling behavior of the sample prepared with Athabasca oil, brine and solids consisting of 100 wt % of sand. These spectra were acquired at 0 hours and the time right after agitation, which was performed after the sample had sat at its stable condition for 24 hours. In this figure, only peaks relaxing at around 1000 ms were observed because the mixture did not contain clay, and loose sand settles very quickly, leading to fast release of free or bulk water. This figure also shows that the spectra were similar at the stability state and right after agitation; thus, this sample represented a fast settling behavior. The spectra did not change significantly even after 3 months, as shown in figure 6.2. The reduction observed in the amplitude values and the small changes in the location of the peaks with time was due to the effect of evaporation of bulk water on top of the sand.

Figures 6.3 and 6.4 present the spectra for the 100 wt % sand mixture of Cold Lake oil and distilled water at different times. In general, these spectra looked very similar to those obtained for the samples containing brine. Comparing the spectra of the two set of samples in greater detail, it appeared that the relative amplitude value for the water peak relaxing at the long relaxation times (i.e. the bulk water peak divided by the total amplitude) seemed higher for the samples prepared with distilled water than for those containing brine; however, the calculated value of both peaks amplitude was determined to be very close. Therefore, it is possible to conclude that salinity did not have a significant effect in the settling behavior of the samples containing 100 wt % of sand in the solids fraction.
In contrast, the setting behavior was distinctly different in the presence of a higher fines fraction or clay fraction. This is shown in figure 6.5 for the mixture containing Athabasca bitumen and brine, with the solids consisting of 95 wt % of clay and 5 wt % of sand before and after agitation. In this case, the peaks obtained at zero hours were once again assumed as the stability state (0 hours) because the sample had not been agitated; consequently, these peaks were taken as points of reference to determine full settling.

At the stability state there was a bulk water peak over 1000 ms, and another signal at shorter relaxation times values corresponding to water relaxing in the small pores of the settled solid. Subsequent to agitation the bulk water peak disappeared, and the entire water signal was relaxing at approximately 50 ms due to the presence of suspended fines. The spectra obtained at later times are shown in figure 6.6.

**Figure 6.1** NMR Spectra of the Mixture Containing Athabasca Bitumen, Brine and 100 wt % of Sand at 0 hours Before and After Shaking

**Figure 6.2** NMR Spectra of the Mixture Containing Athabasca Bitumen, Brine and 100 wt % of Sand at Different Times After Shaking
Figure 6.3 NMR Spectra of the Mixture Containing Cold Lake Oil, Distilled Water and 100 wt % of Sand at 0 hours Before and After Shaking

Figure 6.4 NMR Spectra of the Mixture Containing Cold Lake Oil, Distilled Water and 100 wt % of Sand at Different Times After Shaking

Figure 6.5 NMR Spectra of the Mixture Containing Athabasca Bitumen, Brine, 95 wt % of Clay and 5 wt % of Sand at 0 hours Before and After Shaking

Figure 6.6 NMR Spectra of the Mixture Containing Athabasca Bitumen, Brine, 95 wt % of Clay and 5 wt % of Sand at Different Times After Shaking
After one week, the 50 ms peak split into three smaller peaks, which was an evidence of the presence of settling in the sample (figure 6.6). The peaks found between 10 and 100 ms represent water in settled fines and further clay suspension, and the peak found around 1000 ms corresponds to bulk or free water and sand. This was the signal from water that was now either associated with the large pores in settled sand, or bulk water on top of the clay suspension. The amplitude of the bulk water peak showed a small increment at 2 months but this value did not change significantly in the measurement performed even after 3 months. This indicated that for this sample, a significant amount of settling was still associated with suspended clay even after 3 months of settling and only 20 minutes of agitation.

Figures 6.7 and 6.8 illustrate the settling behavior found for samples containing distilled water and Cold Lake oil and the same solids compositions. From these spectra, the relative amplitude value of the bulk water peaks obtained at 2 and 3 months were calculated and compared with those obtained for the samples containing brine. The relative amplitude of the bulk water for the samples containing brine was less than for the samples prepared with distilled water, but overall the samples are qualitatively similar.

The settling behavior for the sample containing 50 wt % of clay and 50 wt % of sand appeared very similar to the samples prepared with 95 wt % of clay for both qualities of water and oil. The NMR spectra of all samples are presented in figures 6.9 to 6.12. Once again, the higher fines content caused all the water relaxation to be associated with the suspended solids upon agitation. The bulk water peak, which is evidence of solids settling, again occurred only after significant time had passed.
Figure 6.7 NMR Spectra of the Mixture Containing Cold Lake Oil, Distilled Water, 95 wt % of Clay and 5 wt % of Sand at 0 hours Before and After Shaking

Figure 6.8 NMR Spectra of the Mixture Containing Cold Lake Oil, Distilled Water, 95 wt % of Clay and 5 wt % of Sand at Different Times After Shaking

Figure 6.9 NMR Spectra of the Mixture Containing Athabasca Bitumen, Distilled Water, 50 wt % of Clay and 50 wt % of Sand at 0 h Before and After Shaking

Figure 6.10 NMR Spectra of the Mixture Containing Athabasca Bitumen, Distilled Water, 50 wt % of Clay and 50 wt % of Sand at Different Times After Shaking
Finally, a comparison of the settling behavior of all the mixtures after two months is presented in figures 6.13 and 6.14. Even after two months of settling, the spectra of the samples containing clay still have significant peaks in the surface water region, and only small bulk water peaks compared to their properties at the stability condition. This is especially evident in the sample containing 95 wt % of clay in the solids, which was interpreted as samples having a slow settling rate. In the samples prepared with 50 wt % of clays, a shift of the surface peaks towards the right (i.e. longer relaxation times) is observed, which can be considered as a medium settling rate. A fast settling rate was observed in the mixtures containing 100 wt % of sand or 0 wt % of clay, as indicated by the lack of significant signal below 100 ms. The relative amplitude fraction of the free water vs. surface water peaks can also be used to indicate the nature of the settling; after two months, the relative size of the bulk water peak corresponds to the amount of coarse sand in the solids. This can be quantified as differences in the total water relaxation time, which will be discussed in the next section.
The settling experiments performed with synthetic samples illustrated the slow settling of tailings that contain a high fraction of clays. From the spectra after agitation, these samples could be identified as having no strong bulk water signal at early times. In typical process times of less than 24 hours, the settling of these tailings will be minimal. This would lead to poor water recovery in the plant, and very poorly settling tailings ponds. Therefore, in order to address these issues, chemical additives are commonly added to speed the settling.

### 6.2.2 Settling Behavior Analysis Using $T_{2gm}$ Values

The settling behavior of the synthetic tailings samples was also analyzed from the relationship between $T_{2gm}$ values and clay content. The $T_{2gm}$ values found for the synthetic samples as a function of time are presented in the figures 6.15 and 6.16. From these figures, it was apparent that the samples containing 100 wt % of sand had a higher $T_{2gm}$, which corroborated the observation that the settling rate should be faster for these
samples than for those containing 50 or 95 wt % of clay. This was expected because sand particles are larger and denser than clays particles; consequently, settling occurs very rapidly. Moreover, clay particles also contain stronger surface charges, which leads to much more stable suspensions than when only sand is present (Chung, 2007).

The $T_{2gm}$ values for the mixtures prepared with 50 and 95 wt % of clays were found to be very similar; however, the $T_{2gm}$ values of the samples containing 50 wt % of clays were slightly longer due to the contribution from the higher sand fraction in these samples. Additionally, it was observed that after two months the $T_{2gm}$ values for the Cold Lake and distilled water mixtures were similar for Athabasca and brine mixtures, meaning that for this brine, salinity did not have a strong influence on the solids settling. Higher salinity should theoretically lead to faster settling due to smaller electrical double layers surrounding the charged clay surfaces (Isaacs and Chow, 1992; Chung, 2007) but a distinct difference in the settling was not observed in these samples. After 3 months of NMR measurements, the complete settling for the mixtures with 50 and 100 wt % of clay content had not been reached yet, and in fact the $T_{2gm}$ of the systems containing significant clay content were still far from their stable state values, which demonstrates a slow settling.

It is significant that there is a monotonic relationship between the clay content and the water $T_{2gm}$ values. When the solids are settled, this relationship can be used to determine the clay content in the sample (Hum and Kantzas, 2007). In samples with high clay content, however, directly after agitation all of the solids are suspended, and the relationship between the water $T_{2gm}$ and the clay content is lost. It is only over time, with changes in the spectra monitored as in figures 6.15 and 6.16, that the relationship between the clay content and the water $T_{2gm}$ once again becomes evident. This is a major difference between NMR interpretations of suspensions, such as tailings samples, compared to interpretation of oil sand properties.
Figures 6.17 and 6.18 illustrate the behaviour of the water $T_{2gm}$ values through time after shaking all the samples. The highest $T_{2gm}$ values corresponded to the samples containing 100 wt % of sand, followed for the samples prepared with 50 wt % and 95 wt % of clay. In this figure a comparison of the $T_{2gm}$ values at any time shows that the correlation between $T_{2gm}$ and clay content is present even for suspensions, however as the clay content increases from 50 to 95 wt% of the solid, this only leads to a small change in the $T_{2gm}$ values at early times. Eventually, however, the difference in the slope of the $T_{2gm}$ values with time for 95 wt% and 50 wt% clay once again demonstrate faster settling with lower clay content. In this manner, the $T_{2gm}$ values show the same behaviour as what could be observed directly from the amplitudes of the bulk water in the spectra and also from the calculations of the relative amplitudes. It is therefore possible to affirm that the $T_{2gm}$ value could be used as an indication of the quality of solids present in a sample, since this value is directly related to the solids particle size distribution. This parameter can therefore be used in numerical algorithms for analyzing the characteristics of the tailings; visual identification of the spectra properties requires knowledge of how to interpret the spectra, while a simple $T_{2gm}$ analysis can be programmed and used by plant operators without any NMR training.
Figure 6.15 $T_{2gm}$ vs. % Clay Content of the Athabasca Bitumen and Brine Mixture

Figure 6.16 $T_{2gm}$ vs. % Clay Content of the Cold Lake Oil and Distilled Water Mixture

Figure 6.17 $T_{2gm}$ vs. Time for the Athabasca Bitumen and Brine Mixture

Figure 6.18 $T_{2gm}$ vs. Time for the Cold Lake Oil and Distilled Water Mixture
6.3 Settling Behaviour Analysis of Real Middlings Samples

Three real middlings samples were provided by Shell Canada Research Centre in Calgary. These samples were prepared using a batch extraction unit (BEU), simulating a low, mid, and high-grade ore extraction. The grade was defined by the amount of bitumen recovered in the BEU process. Gypsum, or calcium sulphate di-hydrate (CaSO$_4$·2H$_2$O), and a commercial anionic acrylamide copolymer flocculant were also provided by Shell Canada.

6.3.1 Experimental Procedure

Three initial middlings samples from low, medium and high-grade ore extraction were prepared by Shell Canada, at a temperature of approximately 40°C. Each one of the three samples was divided in two subgroups. One subgroup was measured by Shell, under the influence of flocculant, through the use of settling columns. Settling columns are graduated cylinders, allowing for visual observations of the height of the water/solids interface through time. The other subgroup was provided to perform settling analysis using the NMR technique under the influence of flocculant, coagulant and a mixture of both substances.

Each of the three middlings samples provided for NMR analysis consisted of approximately 1 L. During the entire time required for samples preparation, chemical addition and NMR measurements, the middlings were stirred continuously and maintained at 40°C. An initial sample was first taken for NMR analysis of settling without any chemical addition. Subsequently, 200 mL of the middling was transferred into a separate 250 mL beaker. The weight of the beaker was measured before and after the middling was added. Based on the weight and volume of the sample, the addition of the flocculant solution was determined to reach 100 ppm. A sample of 20 g of this middling, containing 100 ppm of flocculant, was agitated and measured in the NMR tool. Subsequently, further chemical was added to the 250 mL beaker to yield 150 and 200 ppm of flocculant, with appropriate NMR samples taken at each stage.
A second 200 mL aliquot of the original middling sample was then transferred into another 250 mL beaker, and dosed with 100 ppm of gypsum powder. Finally, a third 200 mL aliquot was used to generate samples of 100 ppm gypsum with 100, 150 and 200 ppm flocculant. At each level of chemical addition samples were taken for NMR analysis of the settling characteristics, thus in total 24 samples were measured from each middling in the NMR tool. All the samples, including the three original middlings, were measured in the NMR2 tool at 0, 2, 4, 6, 24, 48 hours and one week.

The flocculant and coagulant solutions used during these analyses were prepared based on a standard procedure established by Shell. The concentrations of the chemical additives were also the same as those used typically in the settling analysis performed by the Shell team, so the results obtained should be representative of the behavior of these chemicals in actual plant tailings.

6.3.2 Results of Settling Behaviour of Real Middlings Samples

The settling behavior analyses for the middlings samples were performed based on the water $T_{2gm}$ values and on the amplitude values of the free water peaks and the peaks from clay bound water. All spectra presented represent the behavior of samples after two hours of settling. This time was chosen for comparison, because two hours is sufficient for any dynamic effects of the added chemicals to become evident, while still being less than typical process times. Therefore, if significant changes to the settling properties are evident after two hours, the added chemical has been successful in enhancing water release and recovery.

6.3.2.1 Settling Results of Original Samples

The spectra obtained from the three initial middling samples, without any chemical addition, are shown in figures 6.19 to 6.21. Only one peak at different relaxation times was observed for all original mixtures. Samples No.1 and No.3 presented fast relaxation times, while sample No. 2 relaxed much more slowly. Specifically, the spectra of samples
No.1 and No.3 showed a peak around 100 ms and no bulk water peak, which represents a high content of suspended fine solids. This is similar to the response seen after agitation of the synthetic samples containing 50% or 95% clay, whereby the entire water signal was associated with surface relaxation of the suspended solids. Conversely, sample No.2 was concluded to have a low fines solid content, because its peak was located very close to 1000 ms and there was only a minimal surface relaxation effect on the water signal.

Table 6.1 presents the total water amplitudes, the relative amplitudes for the bulk water peaks and the $T_{2gm}$ values for the three original samples. Based on the total amplitude values, it was confirmed that that sample No. 2 contained the highest water proportion. For similar total volumes, the highest water content is also the sample that will have the lowest solids content, thus the longer relaxation times in sample No. 2 are not only indicative of less fines in the solids, but also of a lower total weight fraction of solids. Comparing the amplitude values of samples No.1 and No.3, sample No.3 had a higher amplitude value, which indicated that it likely had fewer solids than sample No. 1. A first pass inference that could be made, therefore, was that settling would be easiest in sample No. 2, followed by sample No.3 and finally by sample No.1. This inference will be tested through the addition of flocculant and gypsum.

The relative bulk water amplitude is taken to be the water signal greater than 1000 ms. For all the samples, there was no bulk water present, indicating that all of the water was associated with suspended solids, which increased the water relaxation rate. Even sample No. 2, which exhibited a much slower water relaxation, was still less than 1000 ms, so the water in this sample was still associated with suspended solids. Therefore, chemical addition was necessary to settle the solids and reclaim the water in all three samples.

Analyzing the water $T_{2gm}$ values, similar hypotheses were made since it was found that the highest $T_{2gm}$ corresponded to sample No.2, followed by sample No.3 and No.1. Therefore, it was once again concluded that sample No.2 had the lowest clay fraction and that samples No.1 and No. 3 would require more chemical addition to enhance settling.
and water release. Again, the water $T_2$ values were under 1000 ms even for sample No. 2, so even this sample required some chemical addition to recover bulk water.

Furthermore, there was no detectable oil signal in the NMR spectra in any of the three original middlings samples, even using the parameters to detect oil signal. This meant that although the samples may contain oil, its amount was under the NMR detection limits. Therefore, it was expected that the clay-water interactions would govern the settling, so the settling characteristics could be optimized only for water recovery only by altering the properties at the clay-water interfaces.

Table 6.1 Amplitudes and $T_{2gm}$ Values for the Original Three Tailings Samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Total Amplitude</th>
<th>Relative Bulk Water Peak Amplitude</th>
<th>Total $T_{2gm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.469</td>
<td>0</td>
<td>77.634</td>
</tr>
<tr>
<td>2</td>
<td>2.950</td>
<td>0</td>
<td>601.696</td>
</tr>
<tr>
<td>3</td>
<td>2.663</td>
<td>0</td>
<td>126.773</td>
</tr>
</tbody>
</table>

Figure 6.19 NMR Spectra of Tailings Sample No. 1

Figure 6.20 NMR Spectra of Tailings Sample No. 2
6.3.2.2 Effect of Flocculant

Flocculation is a phenomenon that implies the formation of a loose or open network, which may or may not separate macroscopically. This is different from coagulation, in that the aggregation of particles is reversible (Everett, 1972).

In the paste technology a flocculant, particularly medium charged anionic co-polymers of acrylamide and acrylate of high molecular weight, becomes attached to the surface of several solids particles. At the surface, it bridges between particles and thereby forms an aggregate or a floc of solids particles. These aggregates are denser than individual particles, thus they tend to settle much faster than individual particles clays (Masliyah, 2007).

Figures 6.22 to 6.24 show the effect of adding different amounts of flocculant (F), during the first two hours at concentrations of 100, 150 and 200 ppm, over the settling behavior of the three middling samples.
As previously mentioned, sample No.2 had a low solids content; this sped up the water releasing process when different amounts of flocculant were added. This fact was clearly noticed in the spectra because the peaks shifted towards 1000 ms, which is the typical relaxation time of free or bulk water. A good water release was also observed in sample No.1 because a high amplitude peak showed up at around 1000 ms after the addition of flocculant.

According to the relative amplitude of the bulk water peak of the sample No.1, the most effective flocculant dose corresponded to 100 ppm, followed by 200 ppm and 150 ppm. This is also shown by the relative size of the peaks in the bulk water portion of the spectra. A larger bulk water peak, and conversely a smaller surface peak, indicates good settling. The low effectiveness in the settling rate with 150 ppm of flocculant was attributed to the sub-sample taken having a higher solids content. This shows that even for the same grade of oil sand, the effectiveness of the added chemical will be related to the amount of clays present in the sample, so in plant-scale monitoring of tailings settling multiple sub-samples should be taken to properly trend the response to chemical additives.

In the case of the sample No. 2, the order of effectiveness of the flocculant dose was found to be 100, 200 and 150 ppm; although all three compositions were effective for this sample In sample No. 3, although the water peaks shifted to longer relaxation times, no water peak was formed at around 1000 ms, which indicates that flocculant alone was not very effective for facilitating water separation. This observation is significant, especially because the water mass was higher in sample No. 3, and therefore the solids content in this sample was known to be lower. It had been expected, therefore, that settling would be easier to induce in this sample, but this was opposite to what was observed when flocculant was added. In fact, in all three concentrations of flocculant, the water signal is still under 1000 ms, so the water was always still affected by surface relaxation, meaning that the clays had not settled out. Even in samples No.1 and No. 2, although a distinct bulk water peak was generated by the addition of flocculant, the water still appeared cloudy when observed visually. This indicated that there were still some solids suspended
in the water, so even the water that was relaxing over 1000 ms could not be recovered directly for re-use in the plant.

Figure 6.22 NMR Spectra of the Sample No. 1 Mixed With Different Amounts of Flocculant (F)

Figure 6.23 NMR Spectra of the Sample No. 2 Mixed With Different Amounts of Flocculant (F)

Figure 6.24 NMR Spectra of the Sample No. 3 Mixed With Different Amounts of Flocculant (F)
The relative amplitude values for the bulk water peaks found for the three samples as a function of flocculant addition are shown in table 6.2. As previously mentioned, these measurements were taken two hours after the tailings were mixed with flocculant in varying doses, in order to determine if NMR can be used to identify a real-time response to chemical addition. These relative amplitude values show the same behavior as what was observed visually in spectra, but the calculation of the relative amplitude of the bulk water peak allows for a quantification of these observations, and could be programmed into software for interpreting the NMR response.

**Table 6.2 Relative Amplitudes of the Bulk Water Peaks after Two Hours, for Varying Flocculant Addition**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>100 ppm</th>
<th>150 ppm</th>
<th>200 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.856</td>
<td>0.501</td>
<td>0.745</td>
</tr>
<tr>
<td>2</td>
<td>0.977</td>
<td>0.974</td>
<td>0.976</td>
</tr>
<tr>
<td>3</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

The relative amplitudes values of the bulk water peaks for sample No. 2 were very similar for all flocculant concentrations, and were always close to unity. This phenomenon indicated that the addition of a concentration of flocculant higher than 100 ppm was not required to accelerate water release. This could be attributed to the fact that the suspended clay fraction was minimal even in the original sample, as evidenced by the initial high water $T_{2gm}$ value without flocculant addition.

In the case of the sample No. 3, bulk water peaks were only observed after one week and not after two hours as in the other samples. The spectra also showed a large suspended solids peak at approximately 60 ms, which together with the lack of free water indicated that flocculant alone was 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.
Figures 6.25 and 6.26 show the relative amplitude values of the bulk water peaks for the samples No. 1 and No. 2 during one week. In these samples, the largest water release occurred during the first six hours, showing that the flocculant acted quickly and efficiently. After this time, the relative amplitude values started to decrease, indicating a re-distribution of free vs. bound water as the samples approached stability state. By one week the values were constant; even after 3 months, the relative amplitude values for the bulk water peaks were essentially unchanged. The small changes observed in the relative amplitude values at later times were attributed to evaporation effects. It is notable that evaporation occurred the most in the samples that showed the best settling properties; this is yet another indication of improved water release, since the free water can evaporate more easily than water in solids. In the case of sample No. 3, (figure 6.27), a bulk water peak was observed only after one week, which indicated that for this sample, the settling process started to occur much more slowly than for samples No. 1 and No. 2.

Figure 6.25 Relative Amplitude of Bulk Water Peaks vs. Time (h) for Sample No. 1 Mixed With Different Amounts of Flocculant (F)

Figure 6.26 Relative Amplitude of Bulk Water Peaks Vs. Time (h) for Sample No. 2 Mixed With Different Amounts of Flocculant (F)
6.3.2.3 Effect of Coagulant

The coagulation process implies the formation of compact aggregates, leading to the macroscopic separation of a coagulum. In this case the aggregation of particles is irreversible (Everett, 1972).

Gypsum (CaSO$_4$·2H$_2$O) is used in the consolidated tailings (CT) process as a coagulant to aggregate the fine clays; then coarse sand is added to act as the load on the aggregated clays or fines. The combination of calcium and coarse solids enhances clear water generation and sediment consolidation. In this case, the calcium present in the gypsum is the main agent, which leads to the aggregation of fines due to the collapse of the electric double layer and the decrease of surface charge (Masliyah, 2007).

The effect of adding 100 ppm of gypsum (G) on the settling rates of the three middlings samples was not as favorable as in the case of adding flocculant because the amount of water released in the same time was less, in particular for the sample No.1. The relative
amplitude of the bulk water peaks was consistently lower than when flocculant was added. These results are shown in Table 6.3.

**Table 6.3 Comparison of Relative Amplitude Values of the Bulk Water Peaks between Gypsum (G) and Flocculant (F) Addition**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>100 ppm (G)</th>
<th>100 ppm (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.001</td>
<td>0.856</td>
</tr>
<tr>
<td>2</td>
<td>0.791</td>
<td>0.977</td>
</tr>
<tr>
<td>3</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

In the sample No.3, no bulk water peak was obtained during the first two hours, as was also observed in the addition of flocculant. Nevertheless, water release was observed after 24 hours and not after one week, as occurred with the different concentrations of flocculant. This fact suggested that although the flocculant and the coagulant did not cause any effect on the settling behavior of the sample No.3 during early times, gypsum started to act faster in promoting the water release than flocculant. However, when the bulk water amplitude values were compared after one week in sample No. 3, it was found that the amplitude value for the bulk water peak was still higher when flocculant was mixed with the sample.

In general, therefore, it could be concluded that the flocculant worked better than gypsum for promoting solids settling. Figure 6.28 presents the amplitude of bulk water peaks obtained in one week (168 h) for the three middlings samples mixed with 100 ppm of gypsum. When comparing these results against 100 ppm of flocculant in figures 6.25 to 6.27, it is evident that for all three samples, the bulk water amplitude fraction is eventually larger with the addition of flocculant, indicating better settling.
The NMR spectra of the three samples under the effect of 100 ppm of gypsum after two hours are illustrated in figures 6.29 to 6.31. From these spectra, it was also possible to affirm that the highest water trapping in the aggregated solids occurred in the sample No.3, followed by sample No.1 and No.2. The significant bound water signal in all three samples shows that although some free water was generated in the spectra, there was still significant water bound to the coagulated settled solids. In all the samples, the addition of gypsum caused a delay in the relaxation time of the water bound with solids, since the new relaxation time is around 100 ms instead of 10 ms as when flocculant was added. This means that the surface bound water is located in physically larger pores than those present during flocculation. The coagulated clays therefore contain significant water volumes, and the final compaction of the solids was not as good as when flocculant had been added.

Although the NMR spectra showed that was still a significant amount of water trapped in the coagulated solids structure, the free water appeared to be clear, upon visual
inspection. This was in contrast to flocculant alone, in which the free water still looked cloudy. This meant that the bulk water was now much more free from suspended solids, and could be re-used in the extraction process, but significant volumes of water were lost to the pores of the coagulated settled solids. Consequently, although gypsum addition leads to the recovery of clean water, gypsum by itself was not very efficient for enhancing settling and water release.

Figure 6.29 Amplitude of Bulk Water Peaks vs. Time (h) for Sample No. 1 Mixed With 100 ppm of Gypsum (G)

Figure 6.30 Amplitude of Bulk Water Peaks Vs. Time (h) for Sample No. 2 Mixed With 100 ppm of Gypsum (G)
6.3.2.4 Effect of Flocculant and Coagulant Mixture

Some studies have shown that the presence of divalent ions such as calcium and magnesium can assist in the flocculation process, particularly when polymers made of acrylamide and acrylic acid are used as flocculants. This type of polymers has provided the best results so far, taking into account that the flocculation ability of polymers depends on their molecular weight, the number of charge points on the polymer, their concentration in the dispersion, solid particle type and mainly the divalent ions in the aqueous phase (Masliyah, 2007). For this reason, mixtures of gypsum (i.e. calcium) and polymer were both added to the three tailings samples in order to investigate the synergistic effect of the chemicals together. The effect of adding 100 ppm of gypsum and different amounts of flocculent (100, 150, 200 ppm) on the settling rate was studied, after having analyzed the influence over the settling behavior for flocculent and gypsum separately. The spectra of these mixtures after two hours are shown in figures 6.32 to 6.34.
Figure 6.32 Amplitude of Bulk Water Peaks vs. Time (h) for Sample No. 1 Mixed With 100 ppm of Gypsum (G) and Different Amounts of Flocculant

Figure 6.33 Amplitude of Bulk Water Peaks vs. Time (h) for Sample No. 2 Mixed With 100 ppm of Gypsum (G) and Different Amounts of Flocculant

Figure 6.34 Amplitude of Bulk Water Peaks vs. Time (h) for Sample No. 3 Mixed With 100 ppm of Gypsum (G) and Different Amounts of Flocculant
The relative amplitude values for the bulk water peaks found for each one of the samples in the presence of the mixture of coagulant and flocculant are presented in table 6.4.

Table 6.4 Relative Amplitudes of Bulk Water Peaks for 100 ppm of Gypsum and Varying Flocculant Addition

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>(G) + 100 ppm (F)</th>
<th>(G) + 150 ppm (F)</th>
<th>(G) + 200 ppm (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.327</td>
<td>0.660</td>
<td>0.888</td>
</tr>
<tr>
<td>2</td>
<td>0.968</td>
<td>0.983</td>
<td>0.888</td>
</tr>
<tr>
<td>3</td>
<td>0.676</td>
<td>0.724</td>
<td>0.777</td>
</tr>
</tbody>
</table>

Based on these results, it was possible to affirm that the most effective formulation in terms of water release for sample No.1 corresponded to the mixture of gypsum with the highest concentration of flocculant (200pm). With gypsum + 100 ppm of flocculant, the bulk water amplitude fraction is actually lower than with the addition of flocculant alone. For both 150 and 200 ppm of flocculant, however, the combination of gypsum and flocculant led to higher bulk water amplitude fractions than with flocculant alone.

In the case of sample No.2, the best results were obtained with 150 ppm of flocculant. Again, at this optimal concentration the bulk water relative amplitude was marginally higher than the value with flocculant alone. In this sample, it was evident that when the concentration of flocculant was increased, the amplitude of the bulk water peaks actually decreased. This could indicate that the sample already was saturated, so the addition of more flocculant inhibited the water release. Comparing the relative amplitude values for the bulk water peaks obtained during the three experiments in tables 6.2 to 6.4, it was found that the highest amplitude value was obtained with the mixture of flocculant and coagulant, even for this sample that contained low solids. In this sample, although, the improvement in the bulk water relative amplitude is not significantly better, the free water was now clear and free of suspended solids.

In the sample No.3, which did not respond quickly to the addition of flocculant and gypsum by themselves, a faster relaxation time of the surface peaks was observed when
both chemical additives were added, even with the lowest concentration of flocculant (100 ppm). This meant that with both gypsum and flocculant present in the system, settled solids were present at a higher degree of compaction that what was measured for either chemical alone. Most significantly, however, the combination of gypsum and flocculant led to the generation of a well-defined free water peak after 1000 ms at very early times. This was definitive evidence that the combination of chemicals had led to improved settling and water recovery in this sample.

Figures 6.35 to 6.37 illustrate the amplitude values for the bulk water peaks during one week after chemical addition for the three samples. It was possible to observe that in all cases, the chemical additives started to act from very early times and the water release occurred during the first 6 hours; after this time the amplitude values tended to have a constant value.

Figure 6.35 Relative Amplitudes of Bulk Water Peaks vs. Time (h) for Sample No. 1 Mixed With Gypsum (G) and Different Amounts of Flocculant (F)  

Figure 6.36 Relative Amplitudes of Bulk Water Peaks vs. Time (h) for Sample No. 2 Mixed With Gypsum (G) and Different Amounts of Flocculant (F)
Comparing visually the water and solids characteristics in all the samples (figure 6.38), it was observed that the water was clear when flocculant and gypsum were added. Therefore, although the NMR spectra showed good bulk water release in samples No. 1 and No. 2 with the addition of flocculant alone, both chemicals were required in order to obtain clear (solids-free) water. With regards to the settled solids, the compaction was best with the use of flocculant alone, and the solids were most swelled with the addition of gypsum alone. Therefore, the effect of the flocculant appears to be to give optimal compaction to the solids, while the value of gypsum is to coagulate the solids and thus provide a relatively solids-free supernatant water layer. By adding both chemicals, some solids compaction is sacrificed; however, flocculant alone cannot lead to solids settling in all samples, and does not provide clear water. According to these results, the mixture of flocculant and gypsum provided the best solution for clear water recovery and better settling rates.
6.3.2.5 $T_{2gm}$ vs. Time Results

The relation between $T_{2gm}$ and time for all original simples and their behavior in the presence of flocculant, coagulant or both are illustrated in the figures 6.39 to 6.41. The results presented correspond to the three middlings samples under the effect of 100 ppm of flocculant, 100 ppm of gypsum, and 150 ppm of flocculant mixed with 100 ppm of gypsum.

Overall, the $T_{2gm}$ values did not change drastically after 48 hours. This corroborates the previous observation made using the bulk amplitude values, which showed that if the chemical addition was successful, the majority of settling would occur at early times. The figures show that the sample No.2, with less solids content, consistently had a higher $T_{2gm}$ than the samples No.1 and No.3. These last two samples had similar solids content; consequently, their $T_{2gm}$ values were comparable. In sample No. 1, however, the addition of flocculant alone led to a significant increment in the water $T_{2gm}$ values, but sample No. 3 required both chemicals in order for a change to be observed in its $T_{2gm}$ values. In all the cases, the mixture of flocculent and gypsum provided the highest $T_{2gm}$ values, which means the best water release at early times. Comparing the effect of flocculent or gypsum
independently, it was found that flocculent generated a better effect in the settling rate than gypsum.

As was the case in the agitated synthetic samples, the analysis of amplitudes and $T_{2gm}$ values allows for identification of both the initial solids content and also the settling properties, which could be programmed into analysis software so that operators would not need to visually interpret the NMR spectra. High water amplitude values for a given mass of sample are indicative of low solids content in the tailings. The location of the solids (i.e. dispersed or settled) can be identified by the relative amplitude of the bulk water peak, and changes in the overall $T_{2gm}$ of the water with the addition of chemical.

Figure 6.39 $T_{2gm}$ vs. Time for Original Samples and Samples Mixed With 100 ppm of Flocculant (F)

Figure 6.40 $T_{2gm}$ vs. Time for Original Samples and Samples Mixed With 100 ppm of Gypsum (G)
6.3.2.6 NMR Results vs. Sedimentation Columns

NMR results were compared with the data obtained by Shell using sedimentation columns. These columns are graduated cylinders, in which only 100 ppm of flocculant was added to the other three sister middling samples, since this is the standard amount used typically as a baseline for settling analysis. The height of the solids suspension was measured visually over a 24 hour period. Table 6.5 shows the recovery, composition and settling results, obtained by Shell, for the three sister middlings samples.

The clarity of water is a visual (operator dependent) number scale used to characterize the free water phase after 24 hours. A higher number indicates that the water appeared to contain less solids. This measurement is heavily biased to the operator running the test, as shown when the water clarity is compared against the actual measured solids content in the overflow stream in table 6.5. Although the clarity of the water appeared to be different in samples No. 1 and No. 2, the actual solids content in the overflow water is similar. For sample No. 3, however, which did not respond well to flocculant addition,
the visual settling column data corroborates the characteristics of the NMR spectra: namely, the water is given a clarity of zero (indicating no change from its initial stage) and a very high measured solids content in the water.

In general, the percentage of solids in the overflow after 24 hours in the settling columns should be in the order of 0.5 or lower; otherwise this indicates that the addition of flocculant by itself did not work and it is necessary to add gypsum. This result was also observed using the NMR technique, because the sample No.3 mixed only with flocculant presented slower surface water relaxation times at approximately 60 ms and no bulk water peak. This characteristic indicated that another chemical agent was required to be added to improve the settling rate. Therefore, the NMR results are representative of the same physical properties that can be measured in settling column experiments.

Table 6.5 Results of the Other Three Sister Middlings Samples Analyzed in Settling Columns

<table>
<thead>
<tr>
<th>Method</th>
<th>Properties</th>
<th>Sample No. 1</th>
<th>Sample No. 2</th>
<th>Sample No. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dean Stark Results</strong> (average)</td>
<td>% Bitumen</td>
<td>7.41</td>
<td>14.28</td>
<td>7.81</td>
</tr>
<tr>
<td></td>
<td>% Water</td>
<td>6.06</td>
<td>1.93</td>
<td>4.99</td>
</tr>
<tr>
<td></td>
<td>% Solids</td>
<td>86.49</td>
<td>83.89</td>
<td>87.20</td>
</tr>
<tr>
<td><strong>BEU Recovery Results</strong> (average)</td>
<td>Primary recovery</td>
<td>42.01</td>
<td>93.50</td>
<td>63.02</td>
</tr>
<tr>
<td></td>
<td>Secondary recovery</td>
<td>48.80</td>
<td>8.20</td>
<td>28.0</td>
</tr>
<tr>
<td></td>
<td>Total recovery</td>
<td>90.80</td>
<td>101.70</td>
<td>91.00</td>
</tr>
<tr>
<td><strong>Settling Data</strong></td>
<td>Average pH</td>
<td>8.32</td>
<td>8.78</td>
<td>8.36</td>
</tr>
<tr>
<td></td>
<td>Clarity of water</td>
<td>5</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>% Solids in overflow at 24h (w/w)</td>
<td>0.48</td>
<td>0.46</td>
<td>2.47</td>
</tr>
</tbody>
</table>

In addition to the settling measurements, the fluid content in the original oil sand samples was also measured through Dean Stark extraction. These data showed that the samples with high, medium and low oil content were the samples No.2, 3 and 1 respectively. The data from Dean Stark and primary recovery from BEU testing correlate well with the tailings properties observed in the NMR spectra. For instance, sample No. 2, which had a high bitumen content, was generally expected to contain less fines solids (Mikula, 1996).
A sample with lower fines content should respond better to froth treatment, and the recovery was also correspondingly highest in this sample. Furthermore, the presence of fines solids in this middling sample was smaller than for the other two samples, as evidenced by the highest water amplitude for this sample. A tailings sample with low fines content also is expected to settle relatively easily, and this was shown in the highest $T_{2gm}$ values for this sample.

The more interesting results, however, are found in comparing the tailings properties in samples No. 1 and No. 3, in relation to their original oil sand compositions and their frothing recovery factors. Sample No. 3 has a slightly higher total solids content, but overall is very similar to Sample No. 1 in terms of oil and solids content. Additionally, primary recovery is actually higher in sample No. 3 than in sample No. 1, which at first would indicate that the fines content is lower in this sample. Moreover, the total recovery (primary + secondary) is similar in both samples. Therefore, predictions of tailings properties and settling behavior based on the original oil sand properties or the recovery from the frothing process would tend to suggest that sample No. 1 would be the most difficult tailing to recover water from. As shown in the NMR spectra and the data from the settling columns, however, the opposite was true.

In general, the data shown indicate how proper analysis of samples at different parts of the plant could lead to improve process efficiency. For example, if it is known that the bitumen content is high and fine solids are correspondingly low, the sample will respond better to froth technology and will not require as much chemical to be added to settle the tailings. However, samples No. 1 and No. 3 had similar oil content in the oil sand, but very different responses both to primary recovery and to chemical addition to the tailings. This demonstrates the risk of determining tailings process conditions based on empirical correlations from the oil sands composition or the froth response. In many cases these correlations will be valid, but as shown in these samples, this will not always be the case. Instead, real-time measurements of tailings properties are required in order to identify if the chemical additives were successful in settling the solids and recovering solids-free
water. The use of the NMR could allow for these differences to be quickly identified, so the extraction and tailings recovery processes can be optimized.

6.3.2.7 Water Mass Predictions

As mentioned previously, samples of tailings of varying grade were provided, and different levels of chemicals were added to alter their settling properties. NMR measurements were made in all the samples over time, to monitor the effectiveness of the chemical addition on the samples settling. Finally, in order to verify the accuracy of the NMR tool in the water mass predictions, all samples were placed in an oven at 110°C for 24 hours to evaporate the remaining water. The change in mass before and after drying was taken to be the water mass present in the sample, which could then be compared to the NMR predictions.

In the proposed measurement approach, the water and oil content are measured by NMR while the solids are determined by mass balance. The oil content in the samples was found to be under detection limits; thus, it was known that the oil content was low in these samples and was taken as effectively zero in the NMR calculations. Only the spectra obtained using the water parameters were used in subsequent analyses. Figures 6.42 to 6.45 illustrate the differences between the real water content and the NMR water mass predictions for the original samples and for the samples mixed with different concentrations of flocculant, gypsum and the mixture of both. The average absolute errors are presented in table 6.6; these values were in a range of 0.18 to 0.42 g which indicated that the NMR water mass predictions were in general very good.

<table>
<thead>
<tr>
<th>Table 6.6 Average Absolute Errors in Water Mass Predictions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Average Absolute Error (g)</strong></td>
</tr>
<tr>
<td>--------------------------------</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
Figure 6.42 Real Water Mass (g) vs. NMR Water Mass Prediction (g) for Original Middlings Samples

Figure 6.43 Real Water Mass (g) vs. NMR Water Mass Prediction (g) for Middlings Samples Mixed with Different Amounts of Flocculant
Figure 6.44 Real Water Mass (g) vs. NMR Water Mass Prediction (g) for Middlings Samples Mixed with 100 ppm of Gypsum

Figure 6.45 Real Water Mass (g) vs. NMR Water Mass Prediction (g) for Middlings Samples Mixed with 100 ppm of Gypsum and Different Amounts of Flocculant
The similarity between NMR water masses and the water mass values obtained through drying of the samples shows that the NMR spectra were accurate. Since oil content was known to be low, as evidenced by the lack of measurable oil signal, these spectra can therefore also be used as an indication of the quantity of solids present in the tailings. Settling will be affected both by the amount of solids present and also by the nature of the solids (i.e. clays vs. sand). A combination of water amplitude and water $T_{2gm}$ analysis can therefore be used to characterize the settling properties of the tailings.

6.4 Summary

The use of the NMR technique in the analyses of the settling behavior of synthetic and real tailings samples provided fast and satisfactory results. The main conclusions obtained from the synthetic samples were that the bulk water amplitude and the water $T_{2gm}$ values could be used as an indication of the fines content in both settled and agitated samples. Furthermore, the results obtained from the measurement of real tailings samples showed that the NMR technique has potential to be used as an on-site fast tool in the disposition of tailings, since the spectra generated by this technique allowed for the effect of flocculent, gypsum or both to be differentiated. The analysis of the NMR spectra also could be used to establish if it was necessary to add a larger proportion of these chemicals to improve water release. For the tailings samples measured in this study, the use of flocculant provided better than gypsum; however, the settling rates were better with the mixture of both chemical additives. The results from analysis of the samples showed that empirical methods for predicting tailings behavior based on the nature of the oil sand or the froth would not always be accurate. Instead, real-time measurements such as those that could be made using the NMR are required for improved process control and optimization.
CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS

In this thesis, a suite of NMR measurements was initially performed on synthetic samples of oil and water, and mixtures of these two fluids and solids. Synthetic and real tailings samples were also measured. The NMR spectra were interpreted for predicting fluids and solids content, and the settling behavior of the tailings samples. The conclusions, based on the results obtained during this study, are the following:

Development of a Bimodal Compositional Detection Method

1. For samples containing low quantities of viscous bitumen, NMR spectra acquired using parameters to detect both the oil and water in a single measurement are highly inaccurate in terms of the oil amplitude. With these parameters, multiple measurements of the same sample will exhibit significant scatter in the measured oil amplitude, and the relationship between oil amplitude and mass is not very good. When oil and water signals are instead acquired in separate NMR measurements, this leads to a relatively fast overall measurement time, with a much higher degree of accuracy in the oil mass prediction.

2. The Bimodal Compositional Detection Method, which consists of using different CPMG pulse parameters to measure the signals from oil and water separately, may be used to estimate water and bitumen content in synthetic and real tailings samples in approximately fifteen minutes. The solids content is calculated by mass difference.

3. The oil mass measurements in samples containing very low amounts of bitumen are highly sensitive to the electronics and the settings of the NMR tool; therefore, a good calibration and fine-tuning of the NMR machine is an important starting point prior to performing measurements.
4. The bitumen content determinations are strongly dependent on the adequate 
determination of the bitumen amplitude index and on the limitation from noise in 
the signal at early relaxation times. This fact is very important particularly for 
samples containing small amounts of bitumen.

5. The tests performed during the development of the Bimodal Compositional 
Detection Method showed that the mixture of kaolinite and illite with water or 
brine does not affect the water and brine amplitude indexes over time. For settled 
samples at ambient pressures, illite and kaolinite lead to water relaxation times on 
the order of 10 to 100 ms. Montmorillonite clay leads to faster water relaxation 
times, so if this clay is present in high quantities in measured tailings, it can 
potentially lead to problems in determination of the oil content.

Analyses of Tailings Synthetic Samples with Different Mixing Configurations

1. NMR measurements provide the same general level of accuracy in water and oil 
mass predictions for synthetic tailings, under different mixing configurations. 
This meant that the methods of spectrum analysis developed during this study 
could be applied to the predictions of actual tailings samples, where the original 
mixing configuration is unknown.

2. In synthetic tailings samples of 20 g prepared with different mixing 
configurations, the NMR tool was able to detect bitumen in amounts higher than 
0.6 g, with a maximum average error of 0.35 g. Water was also detected in all 
samples with a maximum average error of 0.60 g. The water content in all 
samples was always much higher than bitumen.

3. The bitumen detection limit depends fundamentally on the electronics of each 
NMR tool and on the noise levels that could be affecting the decay data. These 
values need to be determined for each NMR machine used in the characterization 
of tailings. The detection limit is also a function of the chosen pulse sequence
parameters used to acquire the decay data. The values proposed in this study provide an optimized level of accuracy for oil and water mass predictions.

4. The low salinity of the plant brine used in this study does not affect the NMR determination of water content. There is no substantial difference in the behavior of samples prepared with brine, compared to those containing distilled water.

Analyses of Fluid Content in Real Middlings and Tailings Samples

1. Tailings samples are characterized by having a high solids content, particularly coarse grains. The presence of these solids can be recognized in a NMR spectrum because the water relaxation times with this type of solids are between 100 - 1000 ms. Conversely, middlings samples contain less solids; but these are composed mainly by clays and fines. In a NMR spectrum, the presence of this type of solids is identified by faster water relaxation times, between 10 - 100 ms. Therefore, if measuring a blind sample, the nature of the sample (i.e. tailing vs. middling) can be quickly identified through the NMR water measurement.

2. In all of the blind tailings samples, NMR could detect water content with a high degree of accuracy.

3. In samples with very low bitumen content, no NMR signal was measured. In samples with higher oil content, some signal could be identified but the mass predicted was always under 0.6 g of bitumen. Therefore, it was concluded that for very low oil content in tailings, NMR predictions of oil mass cannot be made accurately.

4. The NMR technique may not be valid for analytical measurements of the bitumen content in tailings samples but the simple detection of a large oil signal can serve as a warning that the process in the plant is not operating efficiently, so that the tailings can be sent for subsequent processing.
5. The evaluation of NMR in the analyses of tailings samples requires a comparison between the NMR and Dean Stark results directly on the same samples, and not on sister samples. The heterogeneity present in tailings also means that in plant measurements, multiple samples need to be taken in order to properly characterize the tailings. A single measurement (NMR or otherwise) may not be representative of actual tailings properties.

Analyses of Settling Behavior of Tailings Synthetic Samples with Different Solids Content

1. Variations in the settling characteristics of tailings samples can be studied through the geometric mean relaxation times (T_{2gm}) of water, and through changes of the surface and bulk water peaks in the NMR spectra over time.

2. The geometric mean relaxation time (T_{2gm}) value can be used as an indication of the nature of solids present in a sample, since it is observed that as the sand content increases, the water T_{2gm} value increases correspondingly.

3. For samples containing either 50 or 95 wt% of clay, even after the samples had settled for three months the solids were still mainly in a suspended state, as evidenced by the water T_{2gm} values. Therefore, the water T_{2gm} values can be used not only as an indication of the nature of the solids, but also as an indication of the state of the solids (i.e. settled vs. suspended).

Analyses of Settling Behavior of Real Tailings Samples under the Influence of Flocculant, Coagulant and a Mixture of Both

1. The addition of flocculant and gypsum can lead to dramatic changes in the settling properties of the tailings samples containing significant clay content.
2. The tests performed using real tailings samples showed that when the solids content in a sample is very low, gypsum promotes a faster water recovery than flocculant. Overall, however, flocculant works better than gypsum since in the presence of flocculant less water is trapped in the settled solids, so the final water recovery is higher.

3. While flocculant lead to better settling of the solids, the recovered bulk water still has some low levels of suspended solids present. Gypsum leads to the recovery of solids-free water, but with a high fraction of water trapped in the coagulated solids.

4. The mixture of flocculant and coagulant provided the best solution for clear water recovery and good settling rates in real tailings samples.

5. The NMR technique has potential to be used as an on-site fast tool in the disposition of tailings, since the spectra generated by this technique can be used to differentiate the effect of flocculant, gypsum or both over settling rates. This is observed through changes in the bulk water and clay bound water peaks in the NMR spectra.

6. The NMR spectra can indicate when settling is ineffective and then establish if it is necessary to add chemical aids or even increase the proportion of these substances to improve water release. In this manner, on-site NMR measurements of tailings samples can be used to improve process control and efficiency in oil sands mining and extraction.

7. Oil sands with similar oil and solids content may still respond differently to extraction and recovery processes. Likewise, even tailings that appear to have similar levels of clay content may respond differently to the addition of flocculant and gypsum. Therefore, fast on-site measurements are the best way to monitor
process efficiency, and simple correlations of expected recovery or tailings settling may not be accurate.

8. The NMR technique provides similar results to those obtained using settling columns, which are the typical method used in the oil sands mining industry to analyze tailings settling rates. However, while settling column measurements are taken over 24 hours, the NMR response can be quantified much sooner (i.e. after only two hours).

Recommendations for Further Studies

1. A larger number of real middlings and tailings samples with different grades, in terms of oil and clay content in the original oil sand and also in terms of extraction, need to be analyzed through the NMR technique. This is required in order to create a data base that allow for the establishment of specific characteristics of the tailings, according to the conditions of the oil sands extraction process.

2. Tailings and middlings samples at different temperatures could be analyzed in the NMR tool to determine if significant variations are observed in the NMR spectra, particularly in the relaxation times of the oil. At higher temperatures, the oil signal may be easier to measure and this could improve the sensitivity of the oil predictions.

3. Mature Fine Tailings (MFT) samples with the solids content of 30 %, typically found in the tailings ponds, could be measured in the NMR tool to establish if this technique is able to identify the presence of the gel structure characteristic of these kinds of samples.

4. The settling behaviour of the samples could be also analyzed using other kinds of equipment such as the CT scanner. This could allow for a more detailed study of
the settling of a sample, by means of the observation of the change of the water/solids interface in a sample.

5. A good functioning of the NMR tool (electronics, the fan, etc.) must be ensured from the beginning of the experiments, since this factor generates an adverse effect in the electronics of the equipment. For measurement of tailings, attention should be focused on reducing the noise in the acquired signal, since this can obscure the real signal coming from the oil.

6. The NMR should be tested in an actual environment such as an extraction plant, in order to ensure that the sensitive tuning required for tailings measurements can be sustained in this environment.

7. Software used to process the data obtained from the NMR measurements needs to be written, in order to automatically select the initial and the final points of the oil peak, and to interpret the settling behaviour based on the water $T_{2gm}$ values. In this manner, plant operators could use the NMR tool without having to interpret the spectra manually.

8. Further improvements in the prediction of oil and water content could be possible using a combination of NMR and other measurements. One possibility is to first measure the water content and solids distribution using NMR, and then to add toluene to dilute the oil and separate it from the solids. The oil/toluene mixture could then be siphoned off, and the difference between the mass of the mixture and the original mass of toluene added could be used to infer the oil content. Alternatively, after measuring the initial sample with NMR, the water could be vaporized using microwaves and then the sample could be measured again, with all the remaining signal attributed to hot bitumen.
REFERENCES


A. Kantzas, *On-line measurement of fluid content and fluid properties for the oil and gas industry with low field NMR relaxometry*, 2nd Canadian School of Hydrocarbon Measurement (CSHM), Calgary, AB, Canada, 2004.


