Sedimentation Behaviour of Fine Solids in Hydrocarbon

by

Ana Maria Bianchini Moroni

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

In

Chemical Engineering

Department of Chemical and Materials Engineering
University of Alberta

ABSTRACT

The current bitumen extraction process has an alarming and increasing environmental impact that is forcing the industry to find a better way to produce oil. The solution that is in development is a solvent based bitumen extraction process. The removal of fines solids is still an important issue to solve. This study focusses on the settling behavior of fine solids in diluted bitumen. The settling rate of indigenous fines and bitumen coated silica and clays in diluted bitumen using n-heptane as the solvent. In conclusion, the identity of the particles has an effect in the adhesive forces between particles, even if they are coated with a layer of bitumen. Bitumen extracted fines show a slower aggregation mechanism than silica in n-heptane. The silica particles sedimentation behavior was predictable and correlated to their size, in contrast with what was seen with the clays.

AKNOWLEDGMENTS

First, I would like to thank my supervisors, Professor Anthony Yeung and Professor Qi Liu, for inspiring me and guiding me through this project.

I would like to thank the Institute of Oil Sands Innovation for providing the financial support to conduct this research.

I would like to thank my colleagues and friends, especially Mehdi Omidghane, Amin Karkooti, Zahra Rostami and Leyli Mirmontazeri, for sharing their knowledge, for opening my eyes to their culture and always having encouraging words when I needed them. I also appreciate and value all the support Carolina Sola gave me through this period of my life, showing me what true friendship means.

A special thanks to my family for believing in me, even if that meant sacrifices of their own, pushing me to be better and always carrying me in their heart. At last, I would like to thank Benjamin Bschaden, for his constant appreciation, caring support and immense love, making my days brighter and happier.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1 INTRODUCION

1.1 Alberta Oil Sands and Industry

Oil is a commodity that has a very volatile price thanks to the important role that plays in all aspects of people's lives. The rising demand for oil and the unclear future of the conventional supply sites have put oil sands in the spot light. (1)

In 2013, the world's daily production was 90,332,722 barrels per day, where 21.4% was produced in North America. The countries that are the largest producers of oil are Saudi Arabia, United States and Russia.(2)

Canada, being the third country with the largest reservoir of oil, after Venezuela and Saudi Arabia, has made oil production one of the key industry sectors in its economy. The estimated Canadian crude oil production on 2014 is 589,228.70 [m^3/d].(3) The provinces that contributed to this production were mainly Alberta, Saskatchewan and Newfoundland and Labrador (from offshore installations).(4) The Alberta oil deposits are Athabasca, Cold Lake and Peace River; it is estimated to contain no less than 1.7 trillion barrels, making this area the biggest reservoir of oil in the world.(5)

The oil sands are believed to be formed when the province was over flowed by a tropical sea, many millions of years ago, when marine creatures sinked to the bottom of it. With the right combination of pressure temperature and time, the oil was formed. When the Rocky Mountains were formed, this viscous liquid was drained towards the sands and it got absorbed.(5)

The oils sands are a mixed of approximately 85 wt. % solids like silica and clays, 10 wt. % bitumen and 5 wt. % water.(6)

The bitumen obtained from the oil sands is considered to be heavy oil due to its high molecular mass. In comparison with other types of petroleum, it has high viscosity, density and metal concentration and a low hydrogen concentration in comparison with its carbon concentration.(6) The hydrocarbon class composition is normally used to determine the type of bitumen obtained, this means the concentrations of saturates, aromatics, resins and asphaltenes content found in the oil. This is important when selecting the solvent used in the production process. For example, asphaltenes are soluble in aromatic solvents, like toluene, but not on paraffinic solvents such as n-heptane.(7)

1.2 Aqueous Bitumen Extraction

There are two ways to recover ways to recover oil sands that depending on the depth of the deposit. If the oil sands are close to the surface (less than 75m), they are recovered by open-pit mining, if not the in situ (in place) drilling method is more suitable.

The in situ drilling method has a 60% bitumen recovery. It consists in injecting steam and solvents into the underground wells previously drilled. In consequence, the temperature rises and the bitumen becomes less viscous, allowing it be pumped to the surface.(8)

The open-pit mining, also called conventional method, has a 90% bitumen recovery. The oils sands are excavated using mining shovels, after eliminating the overburden. Then, the sands are crushed into more manageable sizes.

The aqueous bitumen extraction method starts when the oils sands are mixed with warm water and chemical additives in the slurring process. The slurry is transported to the flotation beds, where the bitumen is separated from the sand by agitation and air injection. The sand settles in the bottom and the bitumen is collected by the bubbles of air due to the buoyancy effect, creating an oil-rich froth that overflows at the top of the vessel. (8)

At this point, the froth has water, solids, and bitumen. To eliminate the undesirable material, this flow goes into the Froth Treatment. Organic solvent is injected into this stage to precipitate asphaltenes that the water, sand and fine particles left in the mixture. This results in clean diluted bitumen that goes into the solvent recovery stage to evaporate and recycle the solvent into the process. The clean bitumen is upgraded to a synthetic crude oil and sent to the refineries. Figure 1-1 shows the aqueous bitumen extraction.(9)

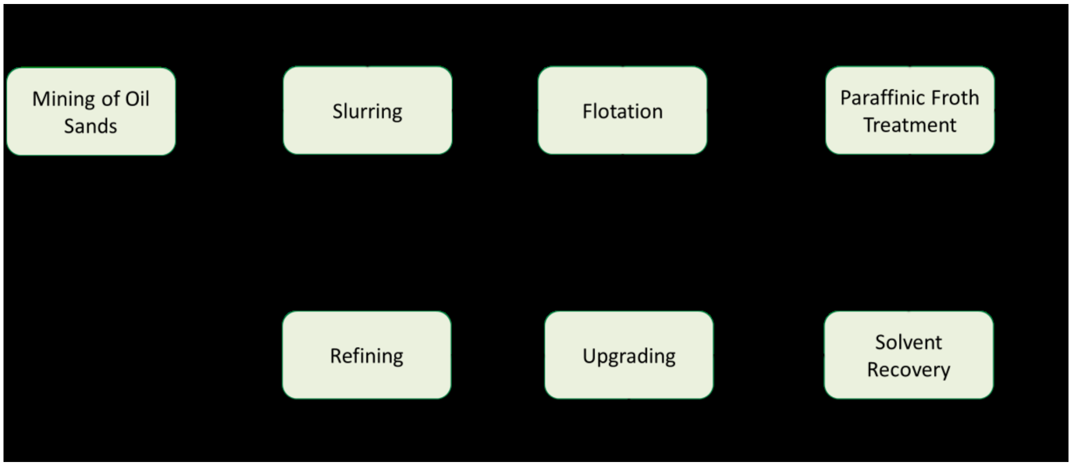

Figure 1-1 Diagram of the current bitumen extraction process.

1.3 Importance of the Research

Current method of bitumen extraction (water-based) has raised environmental concerns, such as the required amounts of water for transportation and flotation, the energy consumed in heating the water, the increasing size and number of tailings ponds and the air pollution from the oil sands projects.(10)

The water based bitumen extraction process uses an alarming amount of fresh water. For every barrel of oil produced, approximately 4 barrels of water are injected in the process mostly taken from the Athabasca River. The oil sands industry consumes more water in a year than the population of Calgary.

Canada's largest growing source of greenhouse gas is the oil sands industry; it contributes with a third of the countries emissions. This is due to the enormous amount of energy used to heat the water in the process explained in the previous section. (10,11)

The waste of the recovery process of bitumen from oils sands is stored on site by forming large tailing ponds containing water, clays, sands, unrecovered bitumen, minerals, etc. This has been proven to be a mayor environmental threat to the ecosystem. These toxic pools are around 50% of the oil mining footprint and their size is growing fast, in 2010 their surface was estimated to be 176 km^2, more than three times their size in 2005. (12)

These alarming environmental concerns are evidence of the urgency to find a more sustainable process for the oil sands industry.

An alternative approach to this process is the non-aqueous (or solvent-based) method of bitumen extraction, involving organic solvents that can be recycled during the process, instead of using huge amounts of fresh water.

The process starts with mining the oils sands, just like in the aqueous bitumen extraction, but instead of incorporating water to prepare slurry, it is diluted with an organic solvent. The solvent of choice has to be able to dissolve bitumen. The flow goes through conventional separation methods, such as filtration or sedimentation, so the large solids can be easily removed. The next stage of the process is to separate the fine solids suspended in the diluted bitumen. The solvent is recovered from the mixture and reintegrated to new mined oil sands. The clean bitumen is sent to the Upgrading and Refining stages. Figure 1-2 shows a diagram of part of the solvent based bitumen extraction. (13-16)

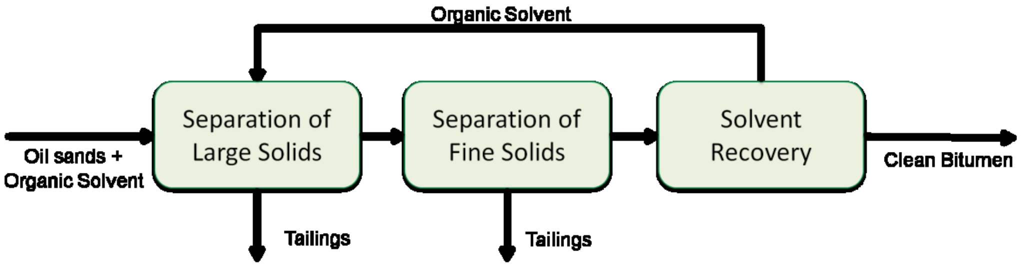

Figure 1-2 Diagram of the solvent based bitumen extraction process.

The challenges of this method are the recovery the remaining solvent and oil trapped between the sand grains and elimination of the fine solids (typically 10 nm to 10 μm in size) that are suspended in the hydrocarbon. These solids are mostly clay materials, with a small fraction being fine silica. The fine solids can cause problem downstream, such as fouling of the catalysts. For the implementation of a solvent based extraction process, these two challenges must be solved.(17-20)

1.4 Objectives of the Study

By providing the right conditions, the fine solids contained in the bitumen can be eliminated by aggregation followed by sedimentation. By adding a suitable organic solvent, the particles can form clusters and settle in the bottom by gravity due to the density difference of the flocculates and the liquid.

The main objective of this study is to analyze the settling behavior of fine solids in a paraffinic solvent. In this research, n-heptane was the solvent studied. It has been seen that using paraffinic solvent in the froth treatment has promising results and efficient in the solids collection process.(21)

A previous study has shown that fine solids coated with bitumen in a paraffinic solution form aggregates due to Van der Walls forces. In this study, the behavior of different sizes of silica and clay particles is analyzed, as well as the behavior of indigenous fine particles found in oil sands. It will supply insight if the identity of the particles is an important variable in their settling behavior, even if they are surrounded by bitumen.(22)

1.5 Thesis Structure

The thesis is developed through 5 chapters. In chapter 2, the background information, of which this project is based, is explained. Chapter 3 provides de the methodology used to conduct the experiments. In chapter 4 the results are provided and discussed. At last, in chapter 5 the conclusions to this research and opportunities of future studies are provided.

2 BACKGROUND

2.1 Bitumen Composition

The oil sands are a blend of approximately 15 wt. % of bitumen, 75 wt. % inorganic material (including silica and clays) and 10% water. (19) Bitumen is a highly viscous liquid that combines different hydrocarbons. It is composed by approximately 83% carbon, 10% hydrogen, 5%sulphur, 1% oxygen, 0.4% nitrogen and small amounts of metals, methane and hydrogen sulphide.(23)

Studies show that the most common clays in oils sands are kaolinite, illite, smectite, chlorite, and mixed layer clay minerals. Even though clay concentrations fluctuate between deposits kaolinite and illite usually predominate.(24, 25)

2.2 Sedimentation and Aggregation

Sedimentation is the effect observed when there are two phases with different densities. The denser phase is surrounded by a lighter one in a gravitational field, for example, a particle in a liquid. Reacting to the forces upon the denser phase, it tends to sediment from the liquid. This can be seen with silica beads dispersed in water, after a short period they sink to the bottom of the container.(26)

As a particle travels through the liquid, the fluid in contact with its surface is dragged with the movement and viscous forces are created. As expected, the solid feel the viscous forces against the movement. These forces depend on the viscosity of the medium, the size and shapes of the particles and the velocity of the particle. When all the forces applied to the solid are balanced the particles has the terminal velocity. Stokes law terminal velocity can be calculated by the following formula.(27)

$$v_s = \frac{d^2(\rho_p - \rho_f)g}{18\mu}$$

Where,

d: is the diameter of a particle

ρ_p: is the density of the particle

ρ_f: is the density of the fluid

μ: is the viscosity of the fluid

This calculation only considers one particle in the system; however, the concentration of solids affects their settling behavior. Hindered settling occurs in the presence of high concentrations of fine solids because the particles movements are affected by the interaction between them and the increment of the frictional forces due to the new flow pattern.(28,29)

Aggregation is called to the process of particles connecting to form clusters. The colloidal stability of the particles controls the agglomerations. Aggregation depends on the ability of particles to collide, favoured by Brownian diffusion, fluid motion or sedimentation, and the ability to collide and stay in that form. Stable colloidal solutions do not flocculate. This type of interactions are subject to short range, less than the particles sizes, and can be attractive or repulsive depending on the surface of the particles and solution. This is an important effect on the separation of fine solids from bitumen. When particles form cluster they settle faster due to a larger mass.(26)

In one hand, if the clusters are formed with the addition of a single particle to the cluster, the shape of it will resemble a sphere, since it is more compact. In the other hand, if the addition is between clusters, the clusters will be less compact and will form faster.(30)

The three collision mechanisms are perkinetic aggregation, orthokinetic aggregation and differential sedimentation. The perkinetic aggregation or Brownian motion consists in small particles in a fluid having a continuous random movement, provoking collision between particles. The orthokinetic aggregation consists in the formation of flocculation due to the motion of the fluid, since the particles collide due to the difference in their velocities. Differential sedimentation occurs when there are particles with different sizes or densities. The particles that settle faster collide with the slower ones. (31)

2.3 Inter-Particle Forces

The forces over the particles dispersed in a liquid can be attractive or repulsive when they come in close proximity. Colloidal forces determine how stable a solution is and how much force is needed to separate them, this means that if the forces are strongly repulsive the aggregates will form in a lower rate and less strength is needed to detach the particles.(26)

2.3.1 Van Der Waals Forces

Van der Wall force is an attractive force between two particles. Three interactions are involved in this force simultaneously: Keesom, Debye and London Dispersion. The Keesom forces explain the interaction between two permanent dipoles. The Debye forces consider the interaction between a permanent dipole and an induced dipole. Finally, the London dispersion forces explain the interaction between 2 induced dipoles. The sum of these three interactions is the Van Der Waals force over a certain particle, and it is relative to the particles sizes and the distance between them.

Considering two spheres with different radius R_1 and R_2, the force is given by the following formula.(32)

$$F_{VDW}(r) = -\frac{A_H R_1 R_2}{6(R_1+R_2)r^2}$$

Where,

A_H: is the Hamaker constant explaining the interaction between the particles and the medium.

r: is the distance between the particles

2.3.2 Columbic Interaction

Two particles that are charged either repel or attract each other under a Columbic interaction. Considering two particles charged with Q_1 and Q_2, which are not in movement, is given by the following formula.(32)

$$F(r) = \frac{Q_1 Q_2}{4\pi\epsilon_0 r^2}$$

Where,

ϵ_0: is the permittivity of free space

r: is the distance between the particles

2.3.3 Electric Double Layer

An electric double layer is formed when a particle is in contact with an aqueous solution. This is caused by the charge induction of electrolytes that are near the surface of the particles. Counter ions are attracted to the electrolytes and co-ions are repelled forming 2 layers from the surface of the particles.

The layer closest to the surface is the Stern layer and the other is called diffuse layer. As the columbic interactions explains, the amount counter ions decrease with the increase distance from the particle`s surface. The electric double layer has a repulsive effect that is relative to the surfaces potential and is inversely proportional to the concentration of electrolytes in the solution.(32)

2.3.4 DLVO Theory

The DLVO theory explains the interaction energy between two particles suspended in a medium by an attractive effect, that destabilize the solution, and a repulsive effect due to the overlapping of the electrical double layers, which prevents aggregation. The sum of these energies is considered to be the total amount of interaction energy.(26)

2.3.5 Cross Bridging

Cross bridging is produced when polymers or molecules are absorbed by the surface of particles suspended in a liquid. The polymers interact with others under the same conditions forming prolonged strings that favour aggregation and precipitation of the particles due to flocculation. (33)

2.3.6 Steric Repulsion

Particles that are suspended in a colloidal substance can adsorb polymers, surfactants or other molecules in their surface, making the solution more stable. The particles interaction depends on the thickness of the layer adsorbed and the medium the particles are in. In one hand, the liquid can either extend the molecules on the surface due to repulsion between strings of molecules causing steric repulsion among particles. In the other hand, the strings can attract each other forming a packed layer in the surface, that's favours the Van der Waals attraction force. (33)

3 TESTING PROCEDURE

3.1 Sample

3.1.1 Particles Identity

The tests were conducted using the same liquid phase but different solids. The solids were obtained directly from a commercial distributor or refined from oil sands.

The different silica particles were bought from Fiber Optic Center Inc. They are considered to be spherical with a density of 2100 Kg/m^3. The diameters specified by the manufacturer are 0.25µm, 0.5µm, 1µm, 2µm and 8µm. This parameter was used to name the samples.

The kaolinite particles bought from Fisher Scientific was named as Kaolinite A, and the particles bought from Sigma-Aldrich was named Kaolinite B. These clays were considered to be non- spherical.

The fine solids were obtained directly from oil sands. The procedure started by combining 150g of oils sands and 100g of toluene using a shaker for 10 min.. Afterwards, the mixture was left to precipitate for one hour. Then, the supernatant was removed with the help of a Syphon that was connected to the suction line. This was sieved with more toluene (50g) and diluted bitumen was obtained. This liquid was centrifuged during 1.5 hours at 4000 rpm at 15°C. At that time, the liquid was removed from the mix and the fine solids where mixed with fresh toluene (50g) to be centrifuged again. At this point, the liquid was clear and the particles were evidently in the bottom of the container. The liquid was removed and the particles were left during 2 days under the fume hood to dry. The last step was to grind the particles with mortar to ensure no attachment between them.

3.1.2 Particle Size Distribution

In order to understand the real diameter of the samples used in this study, the PSD of each sample were obtained using the Malvern MasterSizer 3000.

For the particles purchased from manufacturers the liquid phase was Millipore Milli-Q system water, and for the fine solids obtained from oil sands the liquid phase was HPLC grade Toluene purchased from Fisher Scientific.

A small amount of particles were diluted in the liquid phase and dispersed with 1min. sonication.

3.2 Treatment

3.2.1 Particle Treatment

In this study, the particles are surface-modified with adsorbed bitumen material.

The each type of particles, such as the silica and the kaolinite, were treated to obtain one layer of bitumen in their surface. This is an irreversible coat adsorbed by the surface of the particles that simulates the conditions of the silica and clay particles extracted from oil sand ores. This is done, in order to mimic the real fine particles that are found in oil sands.

Silica and clay particles are hydrophilic. This means that in an aqueous medium particles disperse but in an organic solvent medium (aliphatic or aromatic) the particles aggregate due to Van der Waals forces. A diagram of this effect is shown in Figure 3-1.

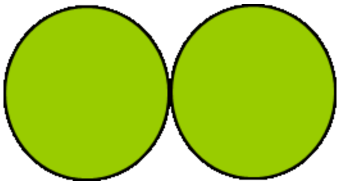

Figure 3-1: Clean Hydrophilic Solids aggregate in any solvent (aliphatic or aromatic)

When the particles are treated with a layer of bitumen, the surface of the particles adsorb strings of molecules that behave like asphaltenes. This is believed due to the behavior that this molecules have in presence of aliphatic and aromatic solvents. If these particles are suspended in an aliphatic solvent, the molecules attract each other, entangling near the surface. This makes the distance between each other shorter favouring Van der Waals forces; therefore aggregation occurs, as shown in Figure 3-2.

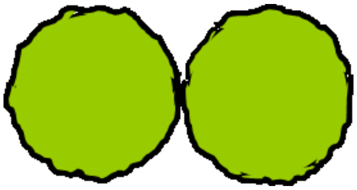

Figure 3-2 Treated Solids aggregate in an aliphatic solvent (i.e. heptane)

If the treated particles are suspended in an aromatic solvent, the molecules repel each other. As a result, the particles have a larger distance between them due to steric repulsion, consequently Van der Waals forces are prevented, as shown in Figure 3-3.

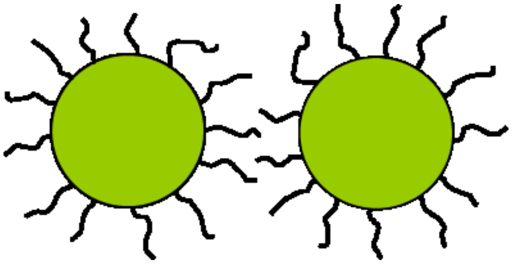

Figure 3-3 Treated Solids don’t aggregate in an aromatic solvent (i.e. toluene)

The indigenous fine solids were not coated with this layer of bitumen, since they were extracted directly from oil sands the thin layer is already in the surface.

For the samples preparation the following steps were taken. First, to ensure that any possible residue in the surface of the particles is removed, the particles received from the commercial distributor were heated on a muffle furnace during 2 hours at 650°C.

Then, bitumen and toluene were mixed in a 1:4 wt. % ratio with the help of a shaker. Afterwards, the clean particles were dispersed in the diluted bitumen mixture at 5 wt. %. To guarantee that all particles are fully wetted, a small amount of liquid (15 mL) is mixed with the particles for 2 min. Next, the rest of the diluted bitumen is added. In order to allow the surface of the particles to absorb this substance, the mixture was left during 24 hour in a magnetic stirrer.

The next step was to wash the particles with fresh toluene to remove all excess of bitumen. This was done by using a centrifuge for 30 min at 4000 rpm. At this point, all the particles are settled and the supernatant was eliminated and substituted by fresh toluene. The new mixture was sonicated for 5 min. and centrifuged again. This was repeated for 6 times.

After discarding the last supernatant, the particles have irreversible coat of bitumen and are still wet by the toluene. They are left under the fume hood to dry during 3 days.

At last, the particles are grinded with the use of a mortar to ensure that particles are not attached to each other.

3.2.2 Maltenes Production

The continuous phase that was used for this study was diluted maltenes. When bitumen is diluted in heptane, it separates in maltenes (low molecular weight) and asphaltenes (high molecular weight). The asphaltenes production is correlated with the type of solvent and the amount of it in the mixture.

The n-heptane used in this study was purchased from Fisher Scientific.

The first step to produce maltenes was mixing the bitumen and heptane in a 1:19 wt. % ratio with the help of a shaker. During the following 2 hours the mixture was a stirred in a magnetic stirrer. The asphaltenes need time to precipitate, so the mixture was left still and untouched for 24 hour. Then, the liquid was emptied in a new recipient and the asphaltenes discarded.

The second step was to eliminate the remaining asphaltenes still remaining in the liquid. With the use of a centrifuge for 30 min at 4000 rpm, again the liquid can be emptied into a new bottle and the asphaltenes can be eliminated.

The maltenes are calculated to be about 65% of the bitumen.

3.3 Testing Method

3.3.1 Sedimentation Balance

In order to obtain concrete, specific and reliable data on the sedimentation rates of the experiments a Kruss K100 Tensiometer was used. The tensiometer has a magnetic mixer incorporated and the sedimentation probe is positions at a certain depth from the liquid surface.

This device registers the total weight of the solids gathered in the probe over a certain period. Figure 3-4 shows an illustration of the probe.

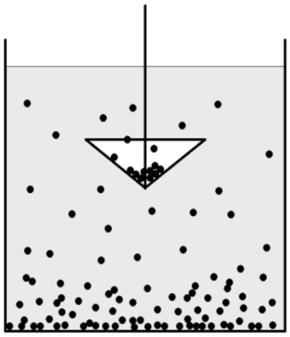

Figure 3-4 Representation of fine solids settling on a sedimentation probe.

In a representative graph of the data obtain by the sedimentation balance, time equals cero when the probe reaches a previously specified depth and the curve has a positive slope until it reaches a point where it changes to a slower settling rate. This shows how the particles aggregate forming clusters and settles until a certain time, when the probe registers a constant weight. This effect can be seen in Figure 3-5.

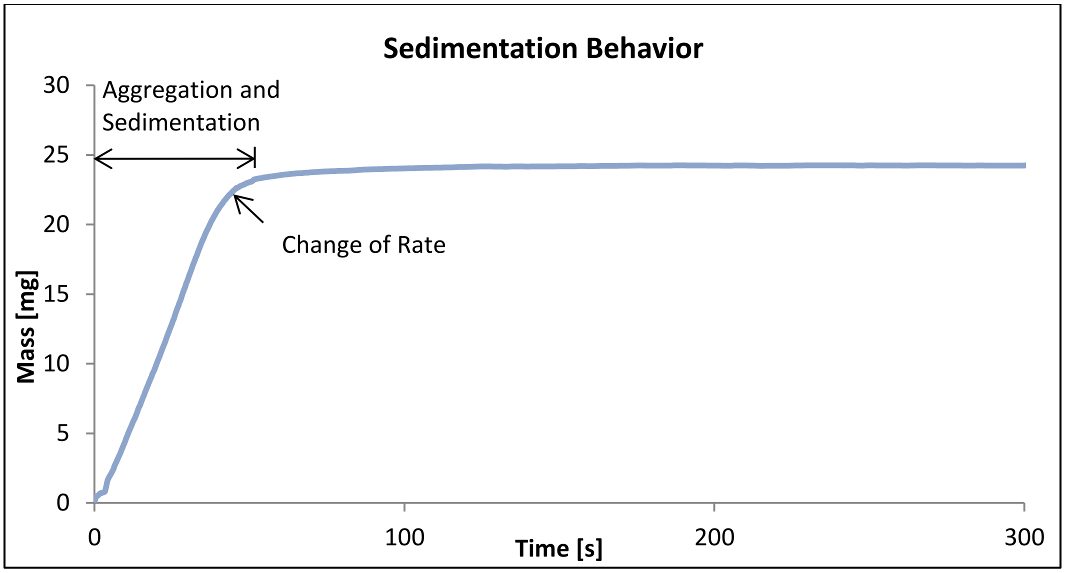

Figure 3-5 Representation of the data registered by a tensiometer.

The acquired data is useful to understand the speed of which the particles aggregate with each other and settle. With this information different particle samples can be compared to understand the behavior of fine solids in the mix of maltenes and heptane.

3.3.2 Concentration

For each type of particles, three different samples were prepared to confirm that the data is reliable and repeatable. The bitumen coated particles were mixed with diluted maltenes in a 1:19 wt. % ratio. To guarantee that all the particles are wetted with the diluted maltenes, a small amount of this liquid (15 mL) is mixed with the particles during 2 min. Then, the rest of the liquid is incorporated and mixed again.

3.3.3 Procedure

When the samples were ready, they were sonicated for 30 seconds to detach any particles that may still be in a cluster. After this step, the samples are put in the tensiometer and the probe is calibrated to find the surface. When the system found the surface, the samples were mixed for 2 min. and then the probe lowered until the depth was reached. At this point, the tensiometer started registering the amount of particles gathered in the probe.

4 RESULT AND DISCUSSIONS

4.1 Particle Size Distributions and Average Length

In order to find the particle size distribution (PSD) of each material, the MasterSizer was used. It provides with the number of particles in each range of sizes. The liquid phase is water for clean hydrophilic particles such as silica and kaolinite, and toluene for fine (hydrophobic) solids extracted from bitumen. This is an important factor in the settling behavior of the particles and enables to compare between samples.

The PSD of the silica samples are shown in Figure 4-1 to Figure 4-5.

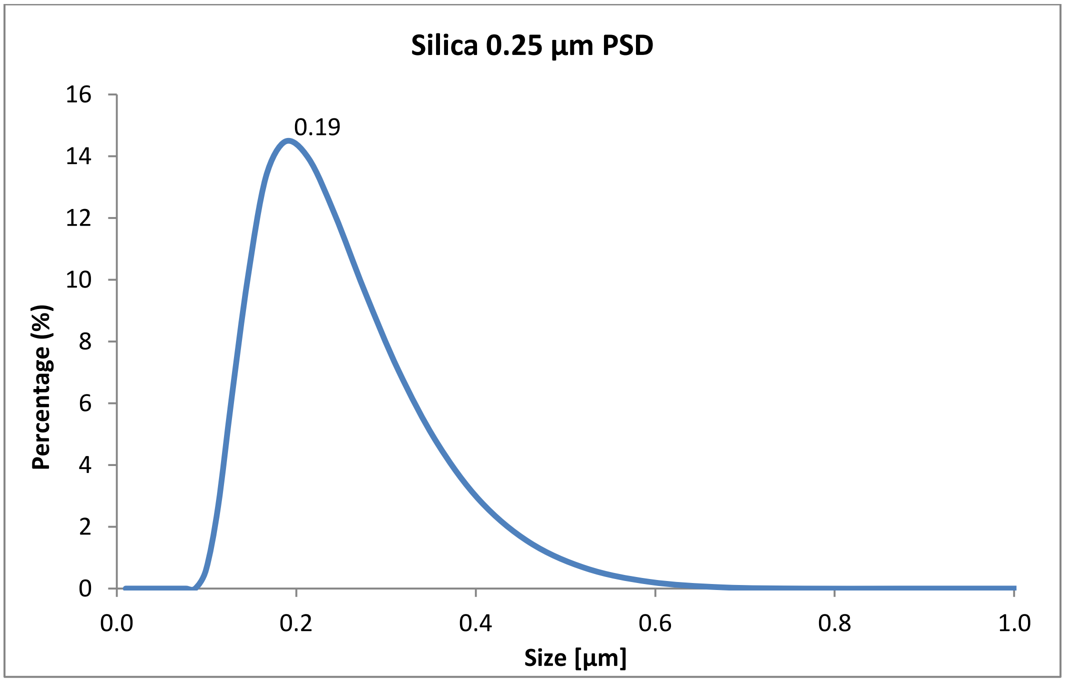

Figure 4-1 Particle size distribution of clean 0.25µm silica dispersed in water.

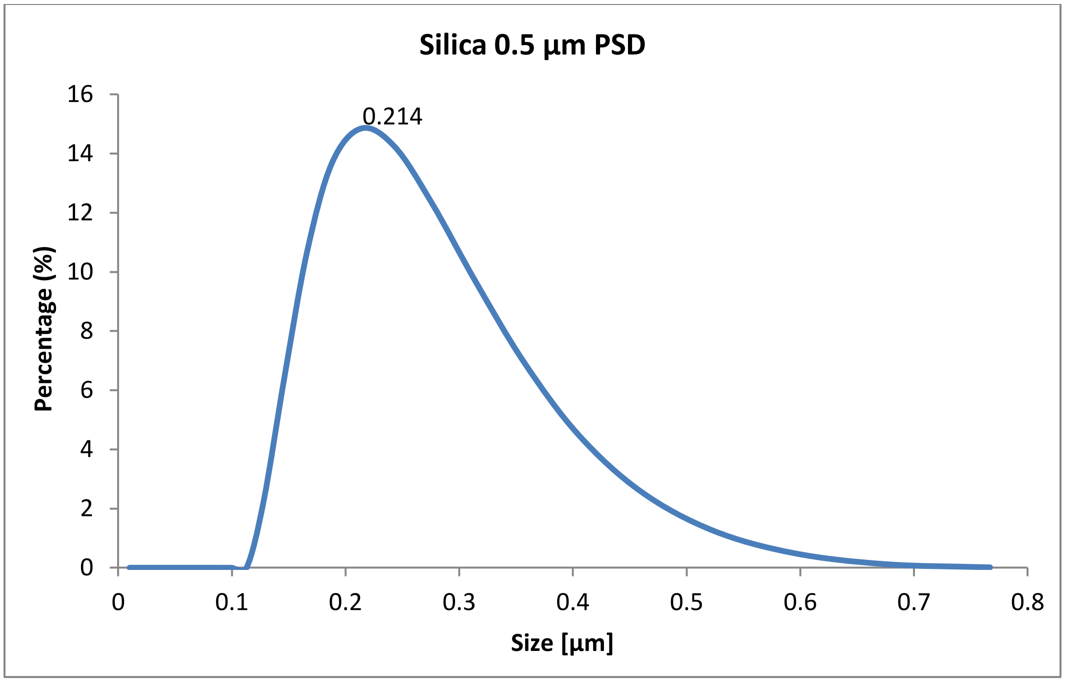

Figure 4-2 Particle size distribution of clean 0.5µm silica dispersed in water.

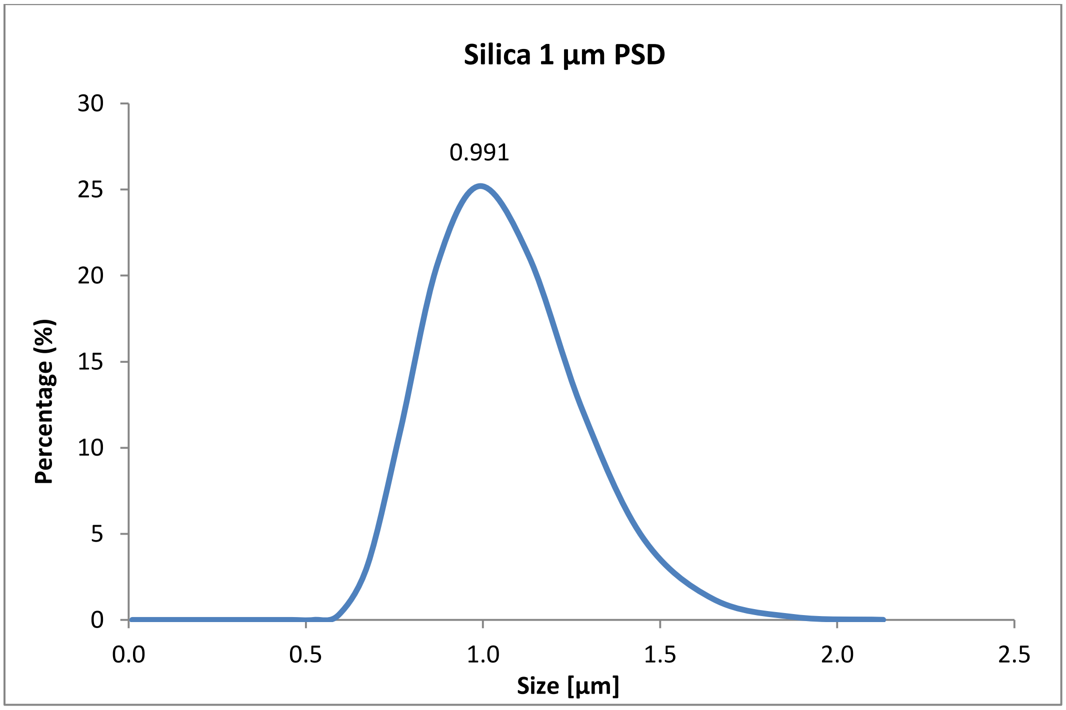

Figure 4-3 Particle size distribution of clean 1µm silica dispersed in water.

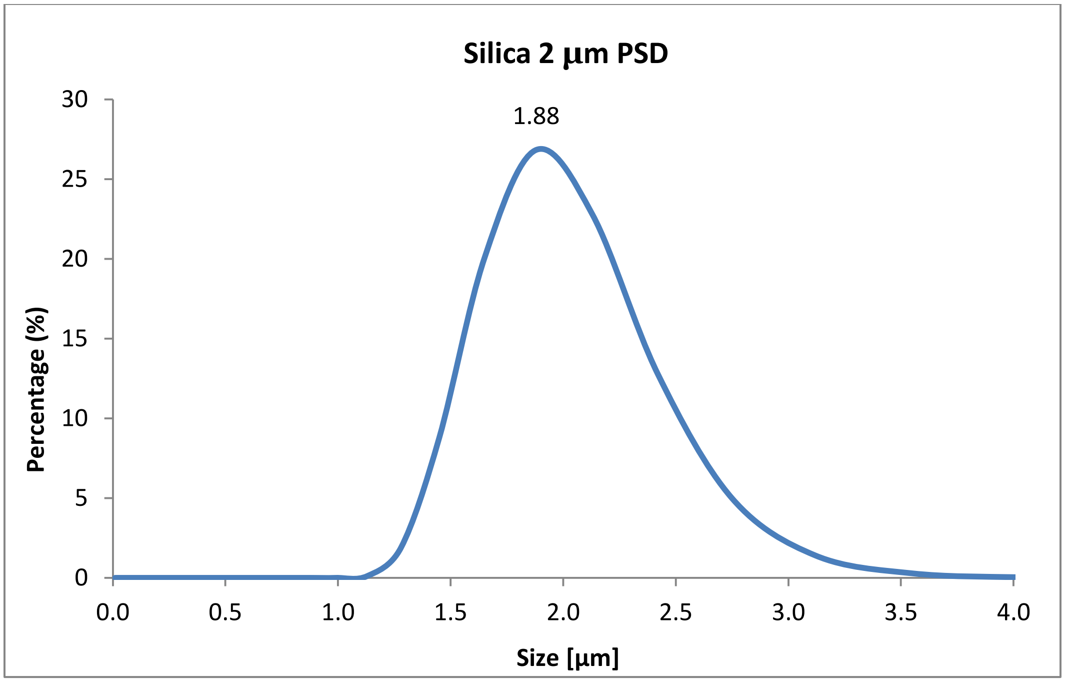

Figure 4-4 Particle size distribution of clean 2µm silica dispersed in water.

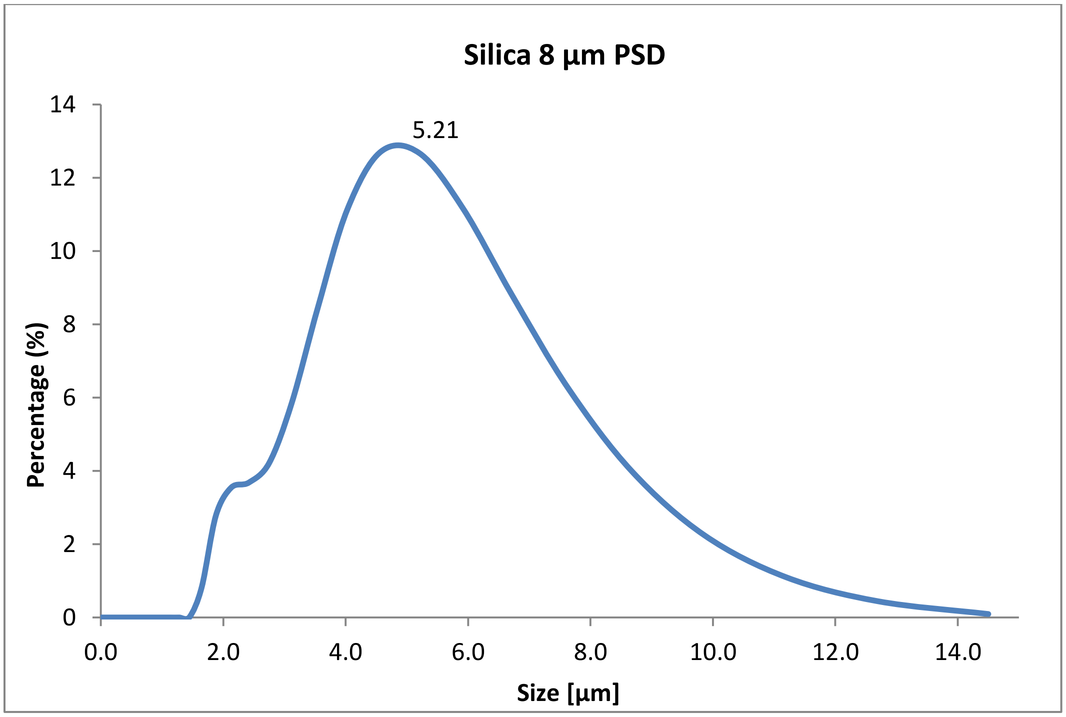

Figure 4-5 Particle size distribution of clean 8µm silica dispersed in water.

As the graphs show, there is difference between what the size of the particles that the manufacturer specifies and the actual PSD. Particles like, the 0.5um Silica has a peak much less than the specified, at 0.21um. And mot all the particles can be approximated to a mono dispersed sample, such as 8um, that it is notorious that the sample has 2 peaks.

The PSD of the clay samples are shown in Figure 4-6 and Figure 4-7.

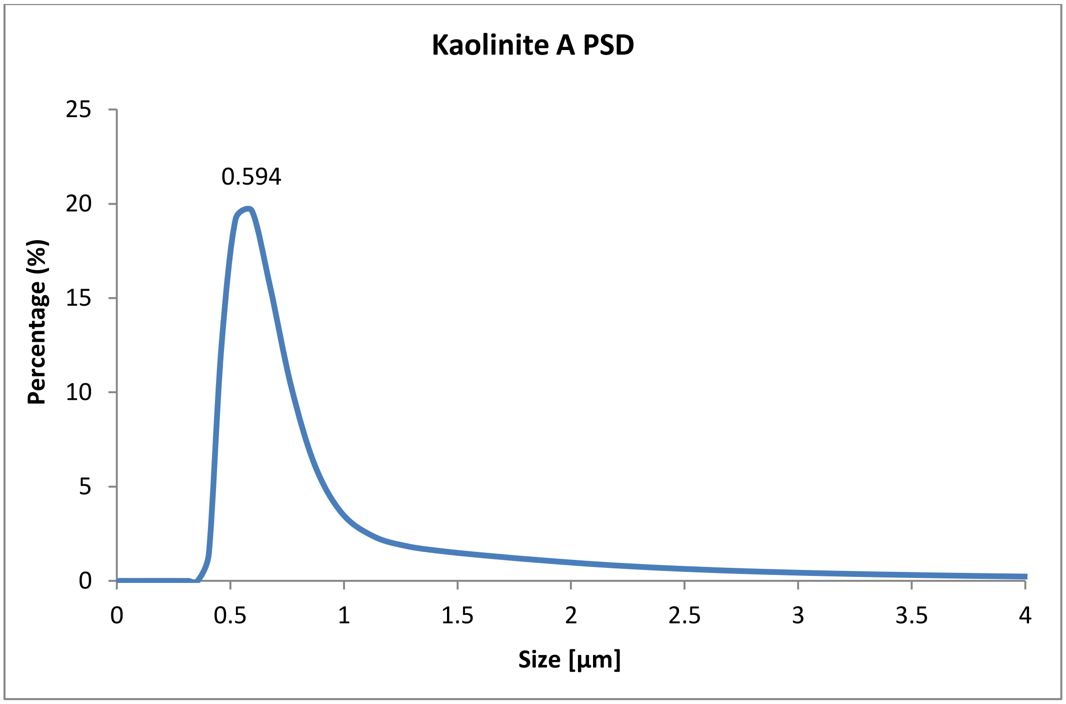

Figure 4-6 Particle size distribution of clean kaolinite A dispersed in water.

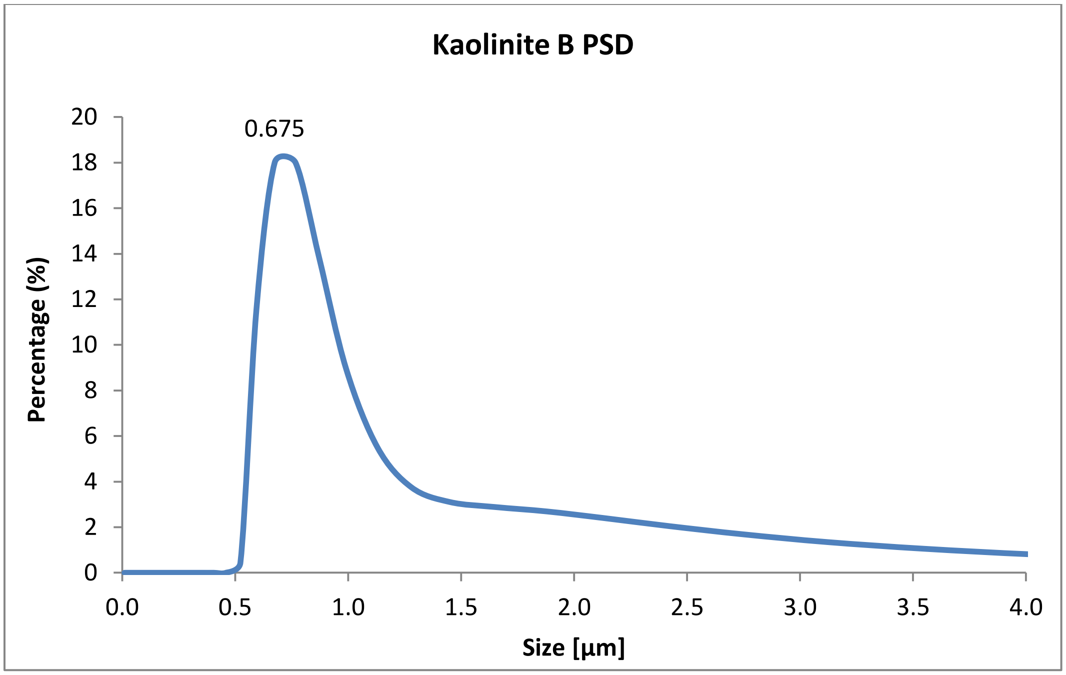

Figure 4-7 Particle size distribution of clean kaolinite B dispersed in water.

In these 2 cases, the manufacturers did not specify any particles size. In both samples the peaks are less than 1um, but Kaolinite A is more mono dispersed than Kaolinite B.

The PSD of the fine solids sample are shown in Figure 4-8.

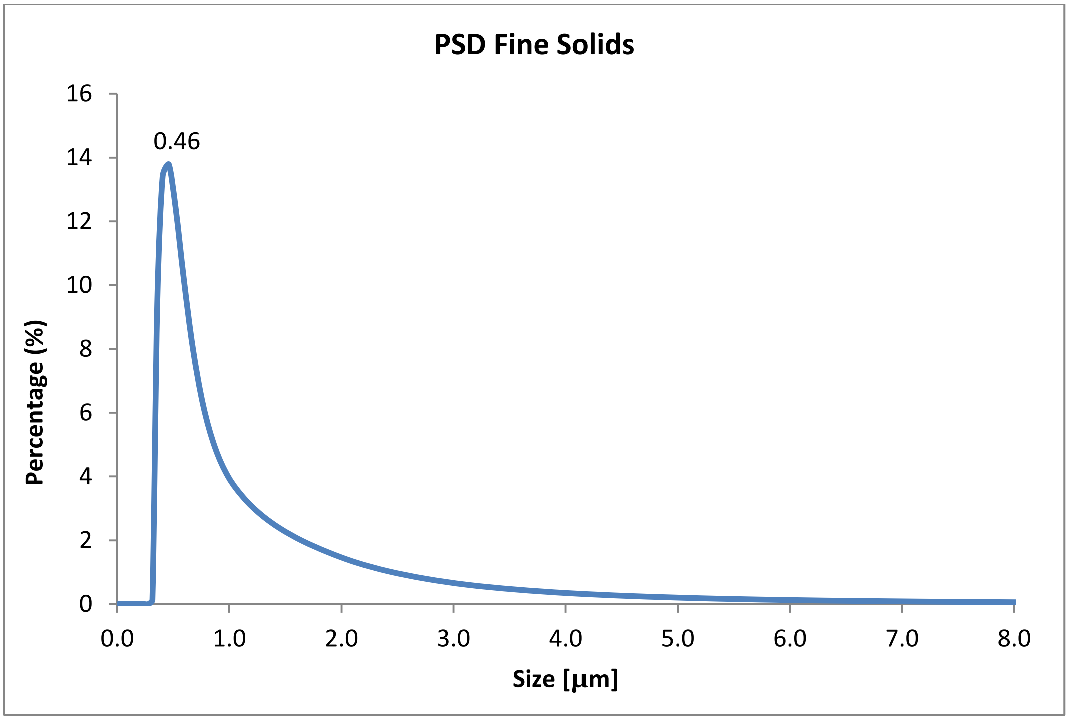

Figure 4-8 Particle size distribution of fine solids dispersed in toluene.

Since the fine solids were extracted directly from bitumen, there was no previous information on the size of the particles. The peak of this PSD is 0.46um approximately.

With the purpose of analyzing and comparing the settling behavior of the samples, an average length has to be calculated. A weighted average was calculated using the following formula.

$$< a > \; = \frac{\int f * a \, da}{\int f \, da}$$

Where,

$< a >$: average length

a: different length of particles in the sample

f: Frequency of particles in each length a

A Matlab code was designed to calculate the average length of each sample. The corresponding codes are found in the Appendix section. Table 4-1 provides the calculations for the samples.

Table 4-1 Samples and their calculated particle length

Particles Identity	**Average Particle Length [µm]**
Silica 0.25µm	0.26
Silica 0.5µm	0.28
Silica 1µm	1.06
Silica 2µm	2.05
Silica 8µm	5.85
Kaolinite A	1.27
Fine Solids	1.57
Kaolinite B	1.99

There are 2 samples under 0.5µm, 4 samples in the rage of 1-2µm and 2 samples in the rage of 2-6µm.

4.2 Settling Curves and Representation of Settling Rates

The sedimentation behavior of each particle can be obtained by analyzing the data registered by the sedimentation balance.

The sedimentation rate is given by the initial slope of this curve. It is known that if y is a linear function of x, the slope-intercept form of the function shows the slope (m) directly.

$$y = mx + b$$

Where,

y: is the dependant variable

x: is the independent variable

m: is the slope of the curve

b: is the y value where the curve crosses the y axis.

In this case, the graphs are a function of mass versus time; therefore, the slope has the units of mg/s.

The sedimentation behavior of each sample is shown in Figure 4-9 to Figure 4-16.

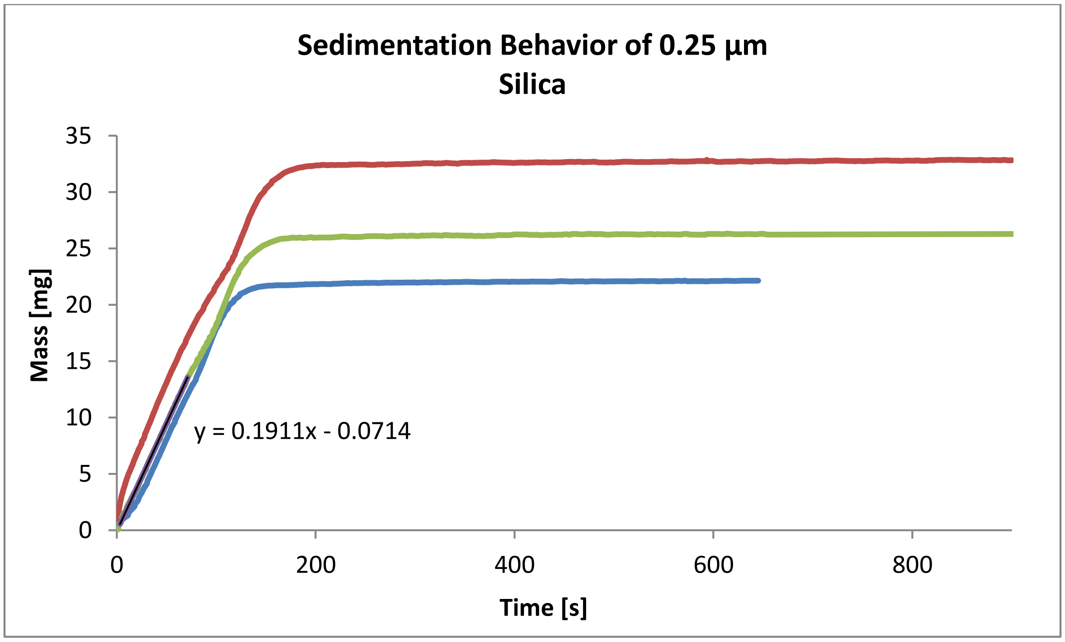

Figure 4-9 Sedimentation behavior of 3 samples of 0.25um Silica in diluted maltenes and their characteristic slope.

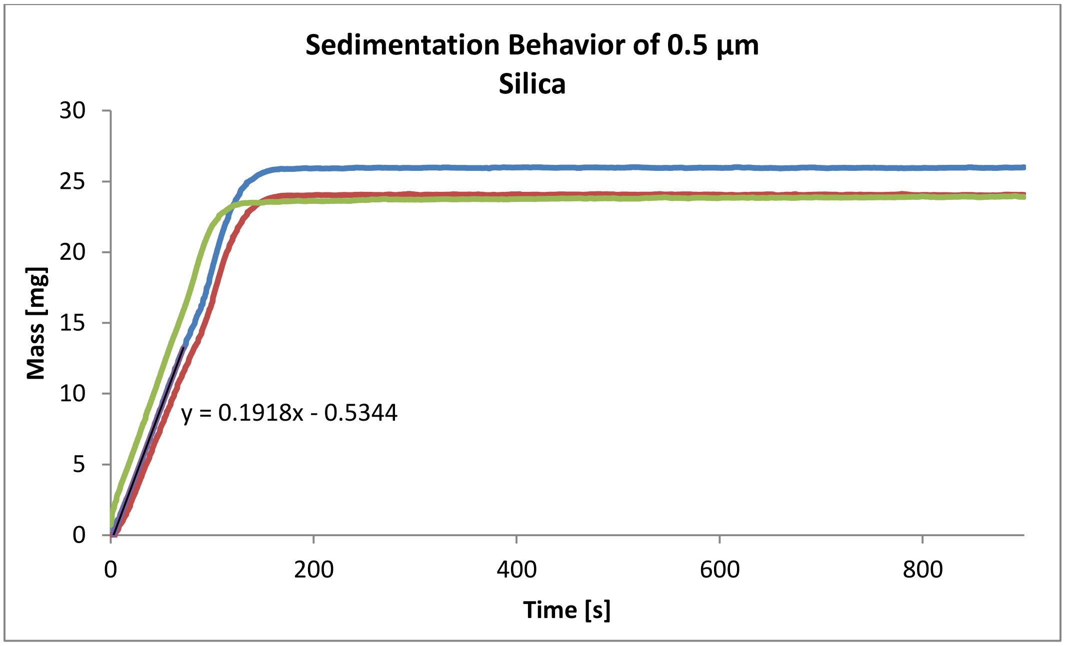

Figure 4-10 Sedimentation behavior of 3 samples of 0.5um Silica in diluted maltenes and their characteristic slope.

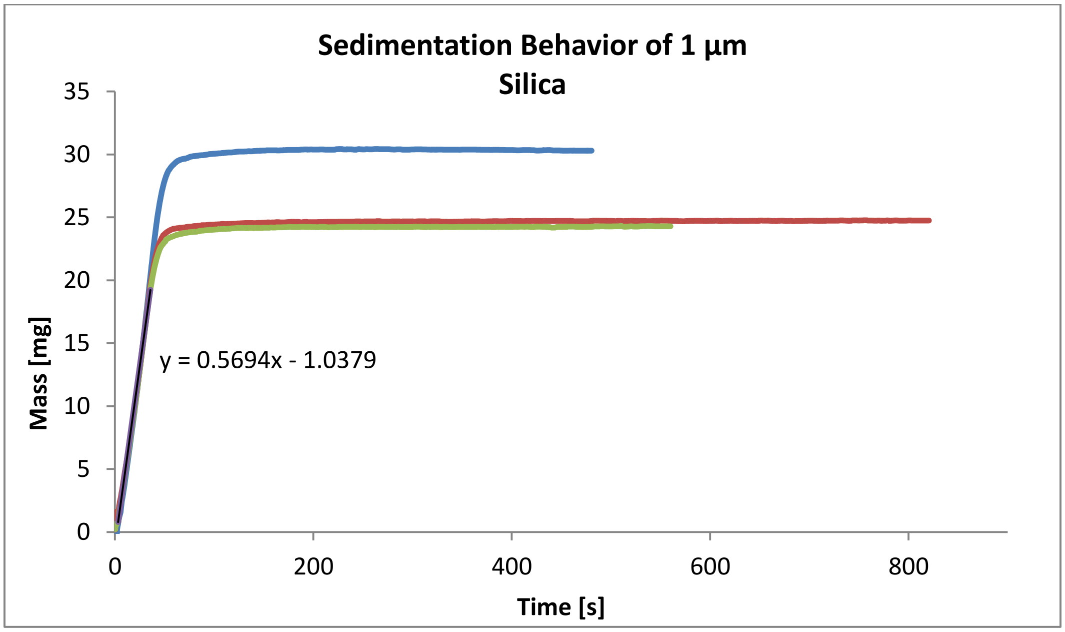

Figure 4-11 Sedimentation behavior of 3 samples of 1um Silica in diluted maltenes and their characteristic slope.

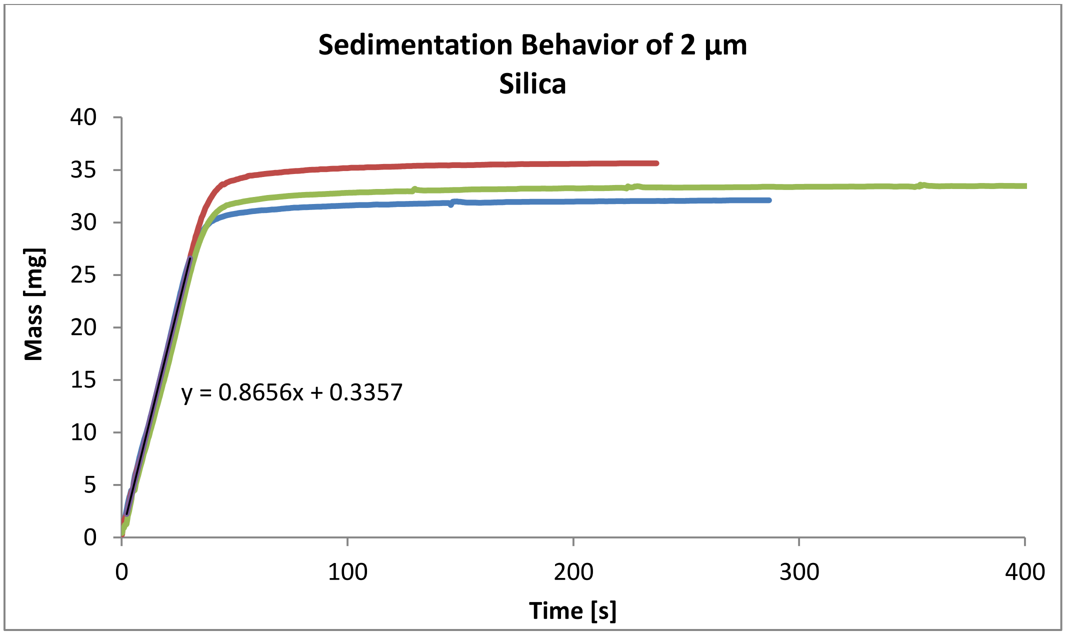

Figure 4-12 Sedimentation behavior of 3 samples of 2um Silica in diluted maltenes and their characteristic slope.

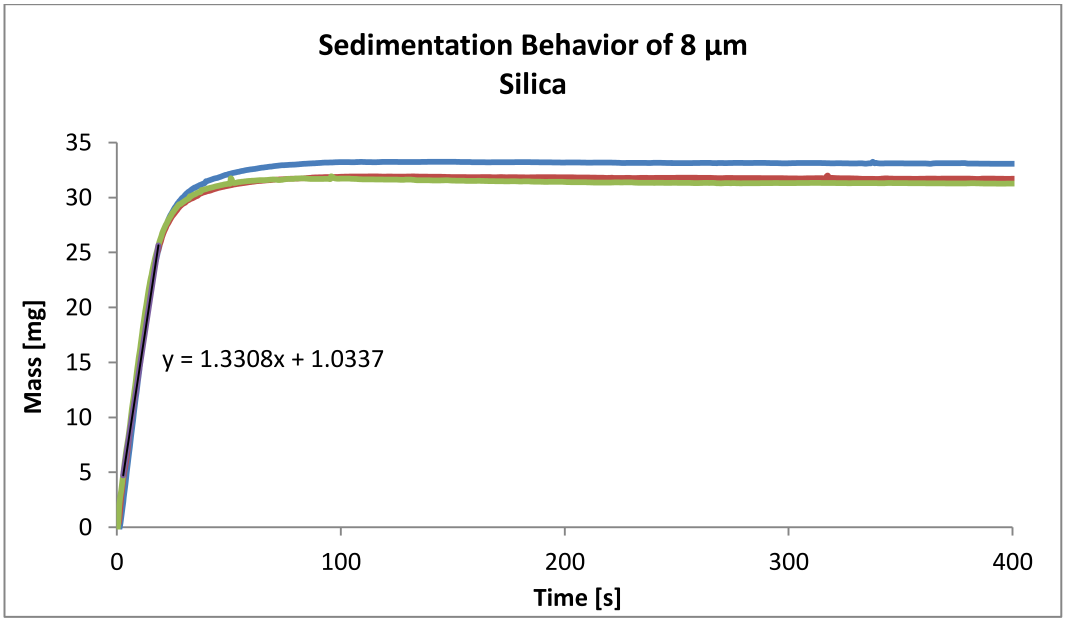

Figure 4-13 Sedimentation behavior of 3 samples of 8um Silica in diluted maltenes and their characteristic slope.

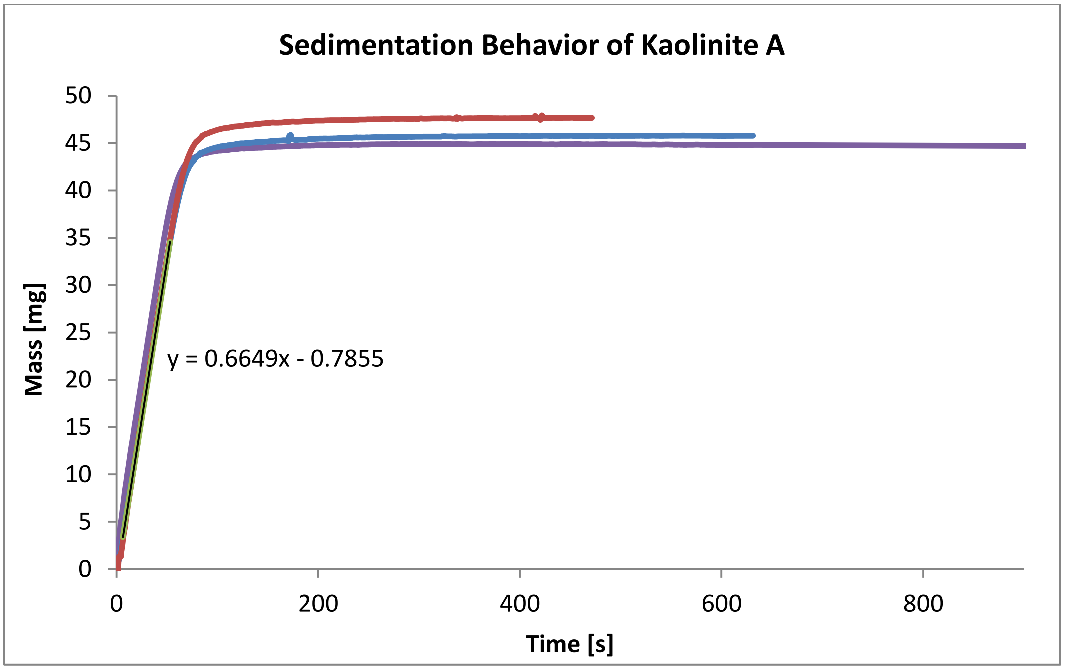

Figure 4-14 Sedimentation behavior of 3 samples of Kaolinite A in diluted maltenes and their characteristic slope.

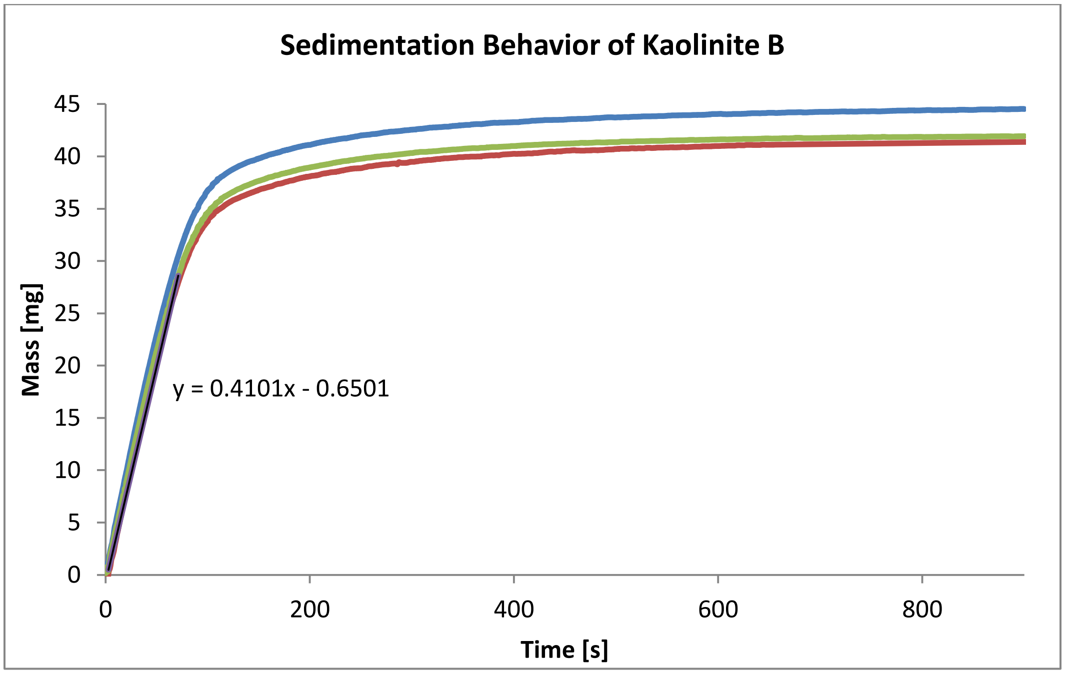

Figure 4-15 Sedimentation behavior of 3 samples of Kaolinite B in diluted maltenes and their characteristic slope.

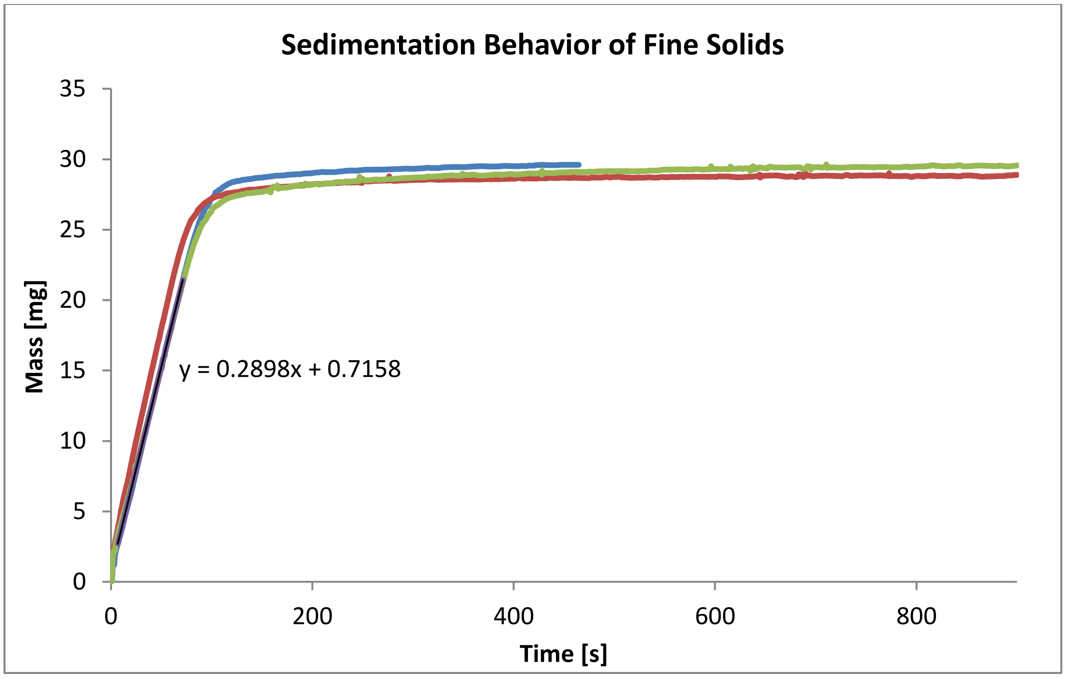

Figure 4-16 Sedimentation behavior of 3 samples of Fine Solids in diluted maltenes and their characteristic slope.

A summary of settling rate of the 8 different samples is presented in Table 4-2.

Table 4-2 Sedimentation rates of each sample

Particles Identity	Settling Rate [mg/s]
Silica 0.25 um	0.1911
Silica 0.5 um	0.1918
Silica 1 um	0.5694
Silica 2 um	0.7944
Silica 8 um	0.8656
Kaolinite A	1.3308
Fine Solids	0.6649
Kaolinite B	0.2898

4.3 Comparison between Samples

The settling behaviors of the particles were compared based in 2 variables, the average length and the sedimentation rate.

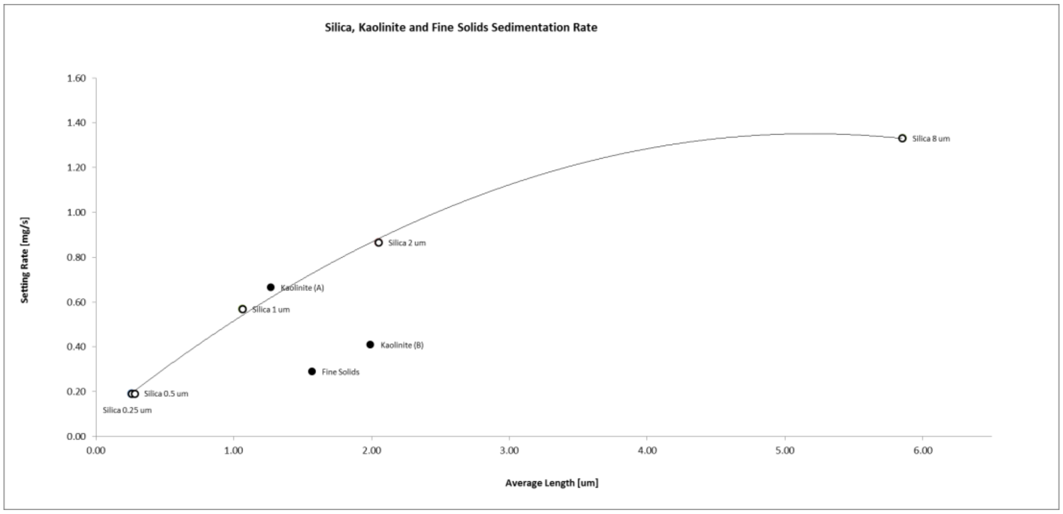

Figure 4-17 Comparison between sedimentation behavior of samples

As **Error! Reference source not found.** shows, the Silica 8µm settles faster than ny other sample. The slowest sample was the Silica 0.25µm, nevertheless, the Silica 0.5µm settles closely to the same rate. This can be explained by the similarity in their particles size. As expected the Silica 1µm is has a faster rate than these 2 samples but is slower than the Silica 2µm.

Stokes law says that, in equilibrium, the settling velocity is proportional to the square of the diameter of the particle. However, the graph shows that the curve relating the particle size and the settling rate curves in the opposite direction. This is because stokes settling velocity considers a system with only one particle and in these experiments there are several particles in the suspension. Consequently, all these particles interact with each other, making the sedimentation behavior more complex due to colloidal interactions. It also evident that there is aggregation because the settling velocity is much faster than expected with stokes law. The settling rate for non-aggregating particles is given by the following formula:

$$\frac{dm}{dt} = \rho v \pi r^2$$

$$\rho = 0.05\,\rho_{heptane} = 34\,\frac{kg}{m^3}$$

Where,

r: Radius of the sedimentation probe

v: Stokes law settling velocity

ρ: Density of the liquid displaced considering 5 wt. % solids.

Calculating the settling rates of the particles with this formula, it can be seen that the silica particles have a much faster settling behavior than expected with stokes law showing that there is aggregation in the system. However, the clays samples show a different behavior than silica. Kaolinite A displays a significantly faster sedimentation rate than Kaolinite B, despite the fact that it has a smaller average length.

The Fine Solids sample has a lower sedimentation rate than both groups of clay particles. In order to compare the silica samples to the fine solids, a curve can be extrapolated to show that fine solids settle in a slower rate than the silica at the same average length.

4.4 Outcome Discussions

In one hand, the silica particles follow the simple principle of the larger the size of the particles the faster it will settle, first by aggregating in clusters and then settling by gravity. This is consistent with the assumption that the silica particles are spherical.

In the other hand, the clay particles show a random behavior. This may be due to the fact that these particles are not spherical and an average length is not a representative variable for their shape. This means that when the particles where measured by the MasterSizer (light scattering system), the results were not representative of the particles diameter. For example the situation could have been that the majority of the particles were measured by their smallest diameter, in the case of the fastest Kaolinite sample, and the slowest sedimentation rate Kaolinite were measured by their largest diameter. This argument is still valid for the fine solids sample.

In conclusion, it is evident that the identity of the particles is an important factor in their sedimentation behavior, even if the particles are coated with a layer of bitumen. Moreover, the average length is a valid variable to compare the behavior of silica particles but not clay particles, because of their non-spherical shape.

5 CONCLUSIONS

5.1 Summary

The growing environmental problems related with the current bitumen extraction process are alarming. The solution seems to be a solvent based bitumen extraction process that will cut back in the water consumption and its related complications. The benefit of the organic solvent is that it can be reused in the process; however, the elimination of fine solids is still a challenge.

The main focus of this study was to comprehend the settling behavior of the fine solids that are naturally found in bitumen, and have a better understanding of how these particles can be removed from it. In order to provide similar conditions as the solvent based extraction process, silica and clay bitumen coated particles and real fine solids were tested. The solvent studied in this research was heptane, and it was used to dilute maltenes as the continuous phase. A tensiometer was used for the testing and obtaining accurate data of the sedimentation rates of each type of particles.

The aggregation and sedimentation behavior of the particles are evidenced by the settling rate obtained by analyzing the data from the experiments.

It was observed that the identity of the particles does matter in the effect of adhesive forces between particles in an organic solvent media. Silica particles showed a predictable settling behavior correlated to their size, in contrast with the clays that had a more unpredictable performance. The fine solids obtained from oil sands show slower settling velocity. This shows that it has a slower aggregation mechanism than silica and some clay particles in n-heptane.

5.2 Recommendations for Further Research

Future studies are necessary to find out more about the sedimentation behavior of particles in bitumen. Research focusing in diverse clay types with different average sizes particles would give specific insight into this subject. Also, a study that centers on a combination of sizes would provide a more realistic view of the process. A more comprehensive view of the Paraffinic Froth Treatment will be achieved by adding these results to the findings of this research.

6 REFERENCES

(1) Woynillowicz D, Serverson-Baker C, Raynolds M. Oil Sands Fever: The Environmental Implications of Canada's Oil Sands Rush. Drayton Valley, Alta.: Pembina Institute; 2005.

(2) US Energy Information Administration. *International Energy Statistics*. Available at: http://www.eia.gov/cfapps/ipdbproject/iedindex3.cfm?tid=5&pid=53&aid=1&cid=regions,&syid=2009&eyid=2013&unit=TBPD. Accessed 5/22, 2014.

(3) National Energy Board of Canada. *2014 Estimated Production of Canadian Crude Oil and Equivalent*. 2014; Available at: http://www.neb.gc.ca/clf-nsi/rnrgynfmtn/sttstc/crdlndptrlmprdct/stmtdprdctn-eng.html. Accessed 5/22, 2014.

(4) Canadian Association of Petroleum Producers. *Canada's Petroleum Resources*. Available at: http://www.capp.ca/energySupply/canadaPetroleumResources/Pages/default.aspx. Accessed 5/22, 2014.

(5) Alberta Goverment. *Oil Sands Overview*. Available at: http://www.history.alberta.ca/oilsands/resources/docs/facts_sheets09.pdf. Accessed 5/22, 2014.

(6) Masliyah, Jacob H., Xu, Z., Czarnecki,Jan A. Handbook on theory and practice of bitumen recovery from Athabasca Oil Sands. Cochrane, Alta.: Kingsley Knowledge Pub.; 2011.

(7) Otto P. Strausz, Elizabeth M. Lown. The Chemistry of Alberta Oil Sands, Bitumens and Heavy Oils. : Alberta Energy Research Institute; 2003.

(8) Canadian Association of Petroleum Producers. *Recovering the Oil*. Available at: http://www.oilsandstoday.ca/whatareoilsands/Pages/RecoveringtheOil.aspx. Accessed 5/22, 2014.

(9) Masliyah J, Zhou ZJ, Xu Z, Czarnecki J, Hamza H. Understanding Water Based Bitumen Extraction from Athabasca Oil Sands. The Canadian Journal of Chemical Engineering 2004;82(4):628-654.

(10) Grant J, Angen E, Dyer S. Forecasting the Impacts of Oilsands Expansion. : Pembina Institute; 2013.

(11) Best J. *Alberta's Oil Sands: Key Issues and Impacts*. 2008; Available at: http://mapleleafweb.com/features/alberta-s-oil-sands-key-issues-and-impacts. Accessed 5/22, 2014.

(12) Giesy JP, Anderson JC, Wiseman SB. Alberta oil sands development. Proceedings of the National Academy of Sciences 2010 January 19;107(3):951-952.

(13) Sparks B, Meadus F. A study of some factors affecting solvent losses in the solvent extraction—spherical agglomeration of oil sands. Fuel Process Technol 1981;4(4):251-264.

(14) Sparks Bd, Meadus FW. A combined solvent extraction and agglomeration technique for the recovery of bitumen from tar sand. 1979;72(1):55-61.

(15) Meadus F, Chevrier P, Sparks B. Solvent extraction of athabasca oil-sand in a rotating mill Part 1. Dissolution of bitumen. Fuel Process Technol 1982;6(3):277-287.

(16) Meadus F, Bassaw B, Sparks B. Solvent extraction of athabasca oil-sand in a rotating mill Part 2. Solids—liquid separation and bitumen quality. Fuel Process Technol 1982;6(3):289-300.

(17) Farnand J, Meadus F, Sparks B. Removal of intractable fine solids from bitumen solutions obtained by solvent extraction of oil sands. Fuel Process Technol 1985;10(2):131-144.

(18) Sparks B, Meadus F, Kumar A, Woods J. The effect of asphaltene content on solvent selection for bitumen extraction by the SESA process. Fuel 1992;71(12):1349-1353.

(19) Hoefele EO, Meadus FW, Sparks BD. Solvent extraction spherical agglomeration of oil sands 1988.

(20) Clifford RK, Hsieh CR. Solvent extraction process for recovering bitumen from tar sand 1987.

(21) Madge D, Garner W. Theory of asphaltene precipitation in a hydrocarbon cyclone. Minerals Eng 2007;20(4):387-394.

(22) Jin Y, Liu W, Liu Q, Yeung A. Aggregation of silica particles in non-aqueous media. Fuel 2011 8;90(8):2592-2597.

(23) Timoney KP, Lee P. Does the Alberta tar sands industry pollute? The scientific evidence. Open Conservation Biology Journal 2009;3:65-81.

(24) Study of bitumen liberation from oil sands ores. Masters Abstracts International; 2010.

(25) Osacky M, Geramian M, Ivey DG, Liu Q, Etsell TH. Mineralogical and chemical composition of petrologic end members of Alberta oil sands. Fuel 2013;113:148-157.

(26) Elimelech M, Jia X, Gregory J, Williams R. Particle deposition & aggregation: measurement, modelling and simulation. : Butterworth-Heinemann; 1998.

(27) Rhodes M. Introduction to particle technology. 2008.

(28) Bürger R, Wendland WL. Sedimentation and suspension flows: Historical perspective and some recent developments. J Eng Math 2001;41(2-3):101-116.

(29) Kynch GJ. A theory of sedimentation. Transactions of the Faraday society 1952;48:166-176.

(30) Gardner KH, Theis TL, Young TC. Colloid aggregation: numerical solution and measurements. Colloids Surf Physicochem Eng Aspects 1998;141(2):237-252.

(31) Gregory J, O'Melia CR. Fundamentals of flocculation. Crit Rev Environ Sci Technol 1989;19(3):185-230.

(32) Israelachvili JN. Intermolecular and surface forces: revised third edition. : Academic press; 2011.

(33) Van der Hoeven, Ph C, Lyklema J. Electrostatic stabilization in non-aqueous media. Adv Colloid Interface Sci 1992;42:205-277.

APPENDIX

Matlab Code to find the Average Length of the Particles

Silica 0.25µm

```
clear all
close all
clc


f = [...
0.004   0.606   2.664   6.153   10.051  13.312  14.481  13.924
12.113  9.648   7.057   4.717   2.836   1.493   0.654   0.215
0.039];

a = [...
0.0876  0.0995  0.113   0.128   0.146   0.166   0.188   0.214
0.243   0.276   0.314   0.357   0.405   0.46    0.523   0.594
0.675];

[dataFit,w] = createFit2(a,f);
spacing = 0.001;
aa =[min(a):spacing:max(a)];
ff = dataFit(aa);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Calculate Integral
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

intAsum = 0;
for i = 1:(size(aa,2)-1)
intA = ((abs(ff(i+1) + ff(i)) )/2)*spacing;
intAsum = intA + intAsum;
end

intBsum = 0;
for i = 1:(size(aa,2)-1)
intB = ((abs(ff(i+1) + ff(i)) )/2)*spacing*((aa(i+1) + aa(i))/2);
intBsum = intB + intBsum;
end

average_size = intBsum/intAsum
```

Silica 0.5µm

```
clear all
close all
clc


f = [...
```

```
0.011   2.264   6.391   10.656  13.677  14.849  14.241  12.320
9.698   6.946   4.488   2.570   1.259   0.495   0.120   0.012];

a = [...
0.113   0.128   0.146   0.166   0.188   0.214   0.243   0.276
0.314   0.357   0.405   0.46    0.523   0.594   0.675   0.767];

[dataFit,w] = createFit2(a,f);
spacing = 0.001;
aa =[min(a):spacing:max(a)];
ff = dataFit(aa);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Calculate Integral
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

intAsum = 0;
for i = 1:(size(aa,2)-1)
intA = ((abs(ff(i+1) + ff(i)) )/2)*spacing;
intAsum = intA + intAsum;
end

intBsum = 0;
for i = 1:(size(aa,2)-1)
intB = ((abs(ff(i+1) + ff(i)) )/2)*spacing*((aa(i+1) + aa(i))/2);
intBsum = intB + intBsum;
end

average_size = intBsum/intAsum
```

Silica 1µm

```
clear all
close all
clc


f = [...
0.001   0.313   3.220   11.008  20.688  25.203  21.114  12.244
4.820   1.214   0.164   0.006];

a = [...
0.523   0.594   0.675   0.767   0.872   0.991   1.13    1.28
1.45    1.65    1.88    2.13];

[dataFit,w] = createFit(a,f);
spacing = 0.001;
aa =[min(a):spacing:max(a)];
ff = dataFit(aa);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Calculate Integral
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

```
intAsum = 0;
for i = 1:(size(aa,2)-1)
intA = ((abs(ff(i+1) + ff(i)) )/2)*spacing;
intAsum = intA + intAsum;
end

intBsum = 0;
for i = 1:(size(aa,2)-1)
intB = ((abs(ff(i+1) + ff(i)) )/2)*spacing*((aa(i+1) + aa(i))/2);
intBsum = intB + intBsum;
end

average_size = intBsum/intAsum
```

Silica 2μm

```
clear all
close all
clc



f = [...
0.049   4.193   10.039  14.571  15.808  13.761  9.751   5.487
2.285   0.673   0.409   1.120   2.523   3.950   4.670   4.341
3.206   1.879   0.870   0.312   0.080   0.011];

a = [...
0.188   0.214   0.243   0.276   0.314   0.357   0.405   0.46
0.523   0.594   0.675   0.767   0.872   0.991   1.13    1.28
1.45    1.65    1.88    2.13    2.42    2.75];

[dataFit,w] = createFit2(a,f);
spacing = 0.001;
aa =[min(a):spacing:max(a)];
ff = dataFit(aa);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Calculate Integral
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

intAsum = 0;
for i = 1:(size(aa,2)-1)
intA = ((abs(ff(i+1) + ff(i)) )/2)*spacing;
intAsum = intA + intAsum;
end

intBsum = 0;
for i = 1:(size(aa,2)-1)
intB = ((abs(ff(i+1) + ff(i)) )/2)*spacing*((aa(i+1) + aa(i))/2);
intBsum = intB + intBsum;
end

average_size = intBsum/intAsum
```

Silica 8µm

```
clear all
close all
clc


f = [...
0.112   1.901   8.807   20.038  26.842  22.787  12.792  4.987
1.403   0.281   0.038   0.002   0.000   0.000   0.000   0.000
0.000   0.000   0.001   0.001   0.001];

a = [...
1.13    1.28    1.45    1.65    1.88    2.13    2.42    2.75
3.12    3.55    4.03    4.58    5.21    5.92    6.72    7.64
8.68    9.86    11.2    12.7    14.5];

[dataFit,w] = createFit2(a,f);
spacing = 0.001;
aa =[min(a):spacing:max(a)];
ff = dataFit(aa);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Calculate Integral
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

intAsum = 0;
for i = 1:(size(aa,2)-1)
intA = ((abs(ff(i+1) + ff(i)) )/2)*spacing;
intAsum = intA + intAsum;
end

intBsum = 0;
for i = 1:(size(aa,2)-1)
intB = ((abs(ff(i+1) + ff(i)) )/2)*spacing*((aa(i+1) + aa(i))/2);
intBsum = intB + intBsum;
end

average_size = intBsum/intAsum
```

Kaolinite A

```
clear all
close all
clc


f = [...0.0152  1.4192  12.3328 19.188  19.6456 15.602  10.3508
6.132   3.5904  2.3648  1.8344  1.5512  1.3144  1.082   0.8644
0.6748  0.5204  0.3992  0.3024  0.2252  0.172   0.1292  0.0952
0.07    0.05    0.03    0.02    0.01    0.01
];
```

```
a = [...0.357   0.405   0.46    0.523   0.594   0.675   0.767
0.872   0.991   1.13    1.28    1.45    1.65    1.88    2.13
2.42    2.75    3.12    3.55    4.03    4.58    5.21    5.92
6.72    7.64    8.68    9.86    11.2    12.7
];

[dataFit,w] = createFit(a,f);
spacing = 0.001;
aa =[min(a):spacing:max(a)];
ff = dataFit(aa);


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Calculate Integral
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

intAsum = 0;
for i = 1:(size(aa,2)-1)
intA = ((abs(ff(i+1) + ff(i)) )/2)*spacing;
intAsum = intA + intAsum;
end

intBsum = 0;
for i = 1:(size(aa,2)-1)
intB = ((abs(ff(i+1) + ff(i)) )/2)*spacing*((aa(i+1) + aa(i))/2);
intBsum = intB + intBsum;
end

average_size = intBsum/intAsum
```

Kolinite B

```
clear all
close all
clc


f = [...
0.18    11.1412 18.1384 18.3272 14.0972 9.154   5.6216  3.818
3.1352  2.886   2.6676  2.362   1.9952  1.6228  1.2832  0.9924
0.7516  0.5556  0.4012  0.2844  0.1964  0.1344  0.0896  0.0616
0.04    0.024   0.0164  0.01    0.01];

a = [...
0.523   0.594   0.675   0.767   0.872   0.991   1.13    1.28
1.45    1.65    1.88    2.13    2.42    2.75    3.12    3.55
4.03    4.58    5.21    5.92    6.72    7.64    8.68    9.86
11.2    12.7    14.5    16.4    18.7];

[dataFit,w] = createFit(a,f);
spacing = 0.001;
aa =[min(a):spacing:max(a)];
ff = dataFit(aa);
```

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Calculate Integral
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

intAsum = 0;
for i = 1:(size(aa,2)-1)
intA = ((abs(ff(i+1) + ff(i)) )/2)*spacing;
intAsum = intA + intAsum;
end

intBsum = 0;
for i = 1:(size(aa,2)-1)
intB = ((abs(ff(i+1) + ff(i)) )/2)*spacing*((aa(i+1) + aa(i))/2);
intBsum = intB + intBsum;
end

average_size = intBsum/intAsum
```

Fine Solids

```
clear all
close all
clc


f = [...
0.14    9.43    13.41   13.79   12.37   10.19   8.02    6.23
4.91    3.99    3.32    2.81    2.38    1.98    1.63    1.31
1.03    0.80    0.61    0.46    0.34    0.25    0.18    0.13
0.10    0.07    0.05    0.03    0.02    0.02    0.01    0.01];

a = [...
0.357   0.405   0.46    0.523   0.594   0.675   0.767   0.872
0.991   1.13    1.28    1.45    1.65    1.88    2.13    2.42
2.75    3.12    3.55    4.03    4.58    5.21    5.92    6.72
7.64    8.68    9.86    11.2    12.7    14.5    16.4    18.7];

[dataFit,w] = createFit2(a,f);
spacing = 0.001;
aa =[min(a):spacing:max(a)];
ff = dataFit(aa);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Calculate Integral
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

intAsum = 0;
for i = 1:(size(aa,2)-1)
intA = ((abs(ff(i+1) + ff(i)) )/2)*spacing;
intAsum = intA + intAsum;
end

intBsum = 0;
```

```
for i = 1:(size(aa,2)-1)
intB = ((abs(ff(i+1) + ff(i)) )/2)*spacing*((aa(i+1) + aa(i))/2);
intBsum = intB + intBsum;
end

average_size = intBsum/intAsum
```

Functions used to find fit

```
%CREATEFIT(A,F)
%  Create a fit.
%
%  Data for 'untitled fit 1' fit:
%      X Input : a
%      Y Output: f
%  Output:
%      fitresult : a fit object representing the fit.
%      gof : structure with goodness-of fit info.
%
%  See also FIT, CFIT, SFIT.

%  Auto-generated by MATLAB on 10-Mar-2014 20:05:11


%% Fit: 'untitled fit 1'.
[xData, yData] = prepareCurveData( a, f );

% Set up fittype and options.
ft = fittype( 'gauss4' );
opts = fitoptions( ft );
opts.Display = 'Off';
opts.Lower = [-Inf -Inf 0 -Inf -Inf 0 -Inf -Inf 0 -Inf -Inf 0];
opts.StartPoint = [18.3272 0.767 0.263069953905792
3.40911248161393 1.28 0.398056190254101 2.32632776360626 2.13
0.497775822756363 1.58217763006627 0.675 0.87415776221354];
opts.Upper = [Inf Inf Inf Inf Inf Inf Inf Inf Inf Inf Inf Inf];

% Fit model to data.
[fitresult, gof] = fit( xData, yData, ft, opts );

% Plot fit with data.
figure( 'Name', 'untitled fit 1' );
h = plot( fitresult, xData, yData );
legend( h, 'f vs. a', 'untitled fit 1', 'Location', 'NorthEast'
);
% Label axes
xlabel( 'a' );
ylabel( 'f' );
grid on


%CREATEFIT1(A,F)
%  Create a fit.
%
```

```
%  Data for 'untitled fit 1' fit:
%      X Input : a
%      Y Output: f
%  Output:
%      fitresult : a fit object representing the fit.
%      gof : structure with goodness-of fit info.
%
%  See also FIT, CFIT, SFIT.

%  Auto-generated by MATLAB on 10-Mar-2014 21:14:56


%% Fit: 'untitled fit 1'.
[xData, yData] = prepareCurveData( a, f );

% Set up fittype and options.
ft = fittype( 'smoothingspline' );
opts = fitoptions( ft );
opts.SmoothingParam = 0.999999999990615;

% Fit model to data.
[fitresult, gof] = fit( xData, yData, ft, opts );

% Plot fit with data.
figure( 'Name', 'untitled fit 1' );
h = plot( fitresult, xData, yData );
legend( h, 'f vs. a', 'untitled fit 1', 'Location', 'NorthEast'
);
% Label axes
xlabel( 'a' );
ylabel( 'f' );
grid on
```