University of Alberta

Effect of Solid Contamination on Stability of Model Oil-Water Emulsions

by

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Abstract

Stabilization of water droplets in froth treatment process results in poor de-watering efficiency and potentially affects final bitumen quality. The purpose of this research is to study the effect of solid contamination by diluted bitumen on water droplet stabilization in water in oil emulsions.

To model froth solids different types of minerals were ground to similar sizes and exposed to solutions of different bitumen concentrations as encountered in froth cleaning process. Complementary surface characterization techniques were used to characterize surface composition. It was revealed that all type of minerals were capable of adsorbing bitumen components when the solid surface was dry.

To mimic the cleaning process, contaminated solids were added to the diluted bitumen and water so that the emulsion formation could be studied and linked with surface properties of solids. The results from this study indicated that partially hydrophobic kaolinite, siderite and silica could stabilize water droplets very well.

Acknowledgments

I would like to take this opportunity to thank my supervisor Professor Zhenghe Xu and Professor Jacob Masliyah for their support and guidance during my Master's program. Their instructions taught me the ability of thinking as an engineer.

I would like to dedicate this thesis to my mother Soroor, and my dear brother Reza.

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1 Introduction

Oil sands of Canada are one of the world largest oil resources with an estimated 1.7 to 2.5 trillion barrels of bitumen in three main regions of Alberta; Athabasca, Peace River and Cold Lake. Bitumen is a heavy, viscous petroleum with high molar mass. It needs to be treated to reduce its viscosity so that it can be pumped and upgraded into synthetic crude oil (SCO) [1].

To extract bitumen from oil sands there are two commercial methods: in-situ production and open pit mining. In-situ extraction of bitumen is performed where the ore is typically buried 200 meters below ground and is too deep to mine [2]. Steam assisted gravity drainage (SAGD) is applied by injecting steam and pumping out the bitumen. Open pit mining method is implemented where the oil sands ore is located within 75 meters of the surface.

In 1920, Clark Hot Water Extraction process (CHWE) was developed by Karl Clark. In this process, the ore mined by shovels is crushed and mixed with hot water and sent to a large primary separation vessel (PSV) via hydrotransport pipeline. The liberated bitumen from sand grain floats to the top, while solids settle to the bottom of PSV as a result of gravity separation and are drained as tailings. This process has been widely used in oil sands with few modifications and improvements. Figure 1-1 shows the general water based extraction process for oil sands [1].

The tailings slurry is discharged to the tailings pond for further treatment and water recycle. The top phase of PSV usually contains 60% bitumen, 30% water and 10% solids by weight and is called bitumen froth. The collected bitumen froth is diluted by solvents to lower viscosity and increase the density difference between the oil and water to allow the oil (organic phase) to be separated from solids and water. Typically two types of solvents are used in commercial operations [3]: naphthenic froth treatment process uses the naphtha as the major solvent and paraffinic froth treatment uses short chain alkane as the diluent. Although paraffinic froth treatment leaves less than 100 ppm water and almost no solid in the oil phase, naphtha diluted froth with about 1% solids and 3% water is still commonly used because this method requires less solvent and is cheaper [2].

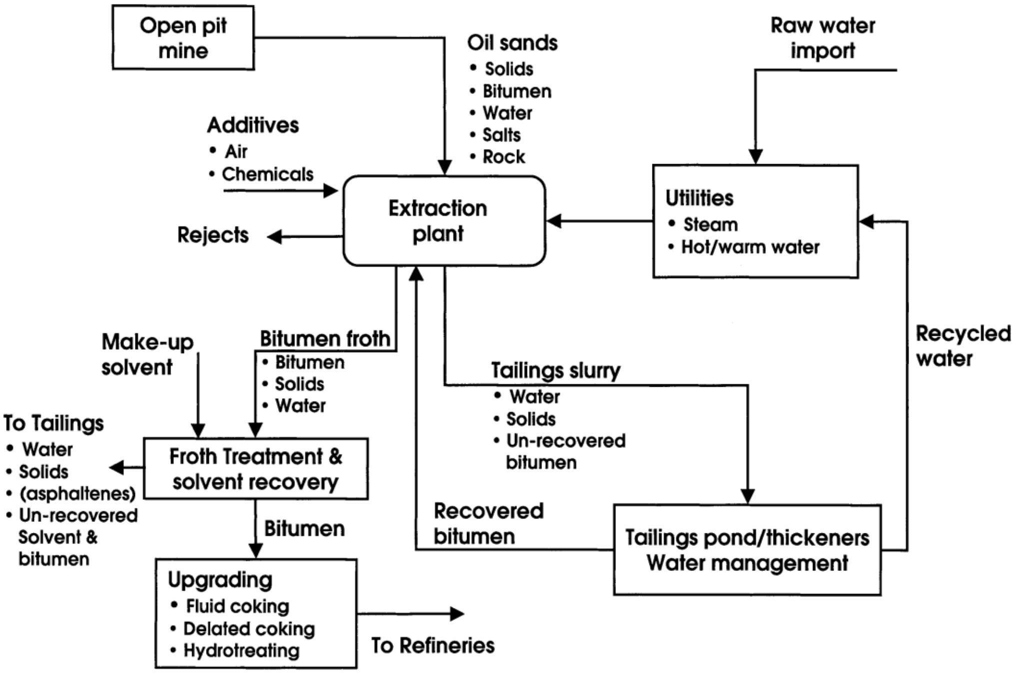


Figure 1-1 Scheme for oil sands processing using water-based extraction processes [1]

The major challenge for producing high quality bitumen in naphthenic froth treatment process is to remove the emulsified water and fine clays because water and solids in bitumen even in small amount would cause damage to downstream facilities [4]. In order to remove the dispersed water droplets and solids in diluted bitumen solution there should be a comprehensive understanding of water droplet formation and stabilization in diluted bitumen in the presence of fine solids.

1.1 Objective of this work

Bitumen contains a variety of compounds, including saturates, aromatics, resins and asphaltenes (SARA) [2]. Although the adsorption of asphaltenes or model components on solids surface has been studied, there is not much work on adsorption of actual bitumen on the surfaces. In this work, the model solids used to study the adsorption were kaolinite, illite, siderite and silica. The first three types of solids are the commonly found and problematic solids in the froth treatment process.

Previous studies on solid stabilized emulsions mostly focused on synthesized silica particles. In this work, treated kaolinite, illite and siderite were used in water diluted bitumen emulsion to study emulsion formation and stability. The bitumen treated silica was also used to compare the emulsion stability results with those from previous works.

1.2 Outline of thesis

This thesis has been divided into six chapters:

Chapter one: this chapter introduces the general background on oil sands process, objectives of this work and the outline of thesis.

Chapter two: this chapter presents literature review on previous studies related to solids isolated from froth treatment in oil sands and the techniques used in their characterization and also the role of these solids in emulsion stabilization.

Chapter three: this chapter discusses the laboratory technique including the material and equipments that were used, are discussed.

Chapter four: this chapter presents solid samples preparation and treatment by diluted bitumen. Then the effect of solid type, solid size, moisture content and bitumen concentration on adsorption of bitumen components on solid surfaces has been studied using different characterization techniques.

Chapter five: this chapter includes the results from emulsions formed using prepared solid samples from chapter four. The study is focused on emulsion stability as a function of solids (hydrophobicity and type), bitumen concentration in oil phase, pH of aqueous phase and the ratio of aqueous phase to oil phase.

Chapter six: this chapter presents the conclusion based on the key parameters from chapter four and five results and recommendations for future work.

2 Literature review

2.1 Bitumen froth treatment

In the bitumen froth treatment process, solvent is added to the froth in order to reduce the viscosity and density of the hydrocarbon, which allows physical separation techniques to separate diluted bitumen from water and solids. To yield this process, the froth comes from two streams. The first stream is the top part of PSV where bitumen content is around 60% by weight. The second stream is PSV middlings that contains about 24 wt% bitumen 59 wt% water and 17 wt% solids. This stream is sent to the flotation cells for aeration, in which air bubbles are injected into the mixture. By attachment of air bubbles to bitumen it is easier for bitumen to float to the top of the cell and separate from water and solids [3].

As mentioned in chapter 1, two main solvents are used to dilute bitumen. Hexane as a short chain alkane is the solvent used in paraffinic froth treatment performed at Shell Albian Sands. This type of solvents precipitates asphaltenes which promotes flocculation of emulsified water and solids as shown in Figure 2-1. After gravity settling, high quality, asphaltene free bitumen is produced.

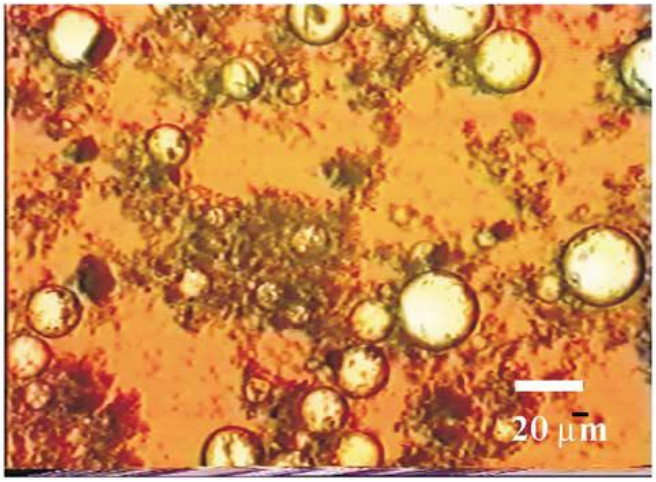


Figure 2-1 Microscopic image of flocs of emulsified water and solids in heptane diluted froth [5]

This method requires a high solvent to bitumen ratio, which increases the cost of operations due to the high cost of solvent. On the other hand, in a typical naphtha-base froth treatment plant, naphtha diluted froth is sent to inclined plate settlers, cyclones or centrifuges to separate water and solids in the stream [3]. The final product contains about 2 wt% water and 1 wt% solids. Emulsified water droplets in the bitumen carry chloride to the up-grader and refineries, which may cause corrosion problems of facilities. CNRL, Suncor and Syncrude use this method for its lower cost of operation [1].

2.2 Bitumen froth components

Froth typically contains water, solids and diluted bitumen. Water in the froth can be in the form of free water and emulsified water [3]. It is easier to separate the free water by any gravity separation method. However emulsified water exists as small water droplets stabilized in bitumen and it is notably harder to separate due to their smaller size and the presence of an interfacial film surrounding the water droplets [6; 7]. Complete de-watering of the oil phase is limited because water droplets in the froth are small and stabilized by:

- asphaltenes [8; 9]
- natural surfactants [6; 10]
- solids [11; 12]

Further complications may arise since in complex multiple emulsions form at oil water interface in separation vessels [13].

2.3 Solids in bitumen froth

Particle size distribution of solids in bitumen froth is associated with different operation parameters in the extraction process; such as slurry velocity in hydrotransport pipelines, temperature and chemistry of operations. The terminology that is employed in oil sands industry for “fines” is the fraction of solids smaller than 44 μm. The percentage of fines in the ore is one factor to evaluate processability of an ore, which describes how much bitumen is recoverable in the froth [2]. Figure 2-2 shows the particle size distribution in different streams [14]. It seems that most of the fines tend to follow middlings and froth. “Clays” are described as the particles of less than 2 μm “equivalent spherical diameter”. At this size, clays in oil sands are often troublesome due to their high surface area to volume ratio (specific surface area) which makes them active components in the system.

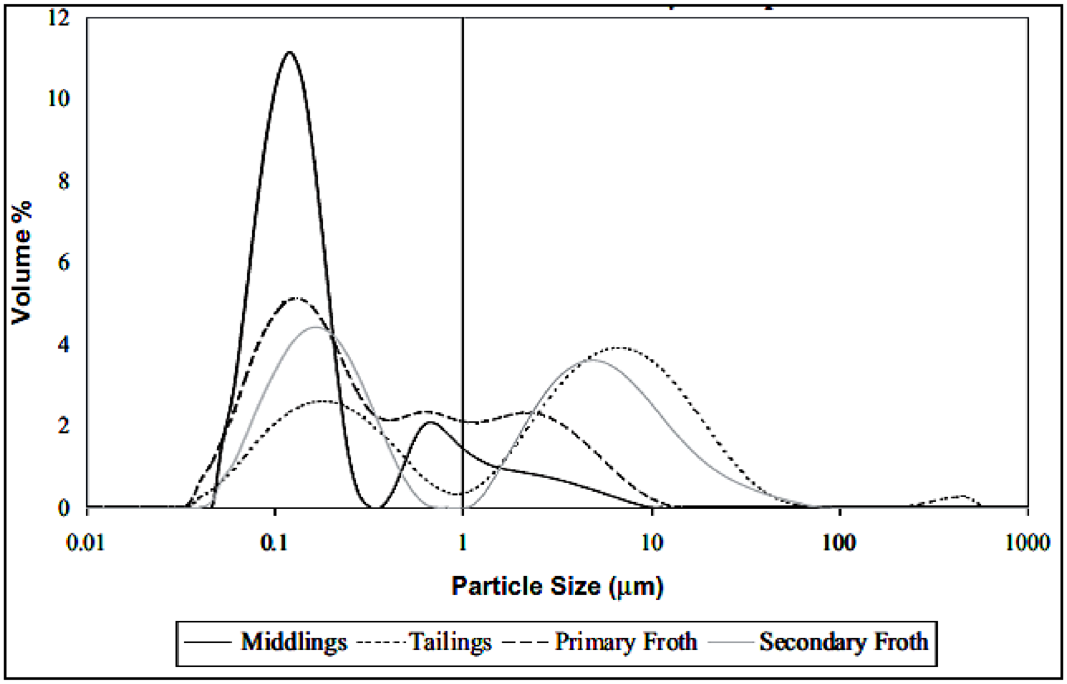


Figure 2-2 Particle size disturbution of different streams [14]

As seen in Figure 2-3 the main clay fraction of solids in oil sands contains clay minerals but it also includes other fine materials such as rock flour and fine metal oxides. According to the international association for the study of clays (AIPEA) nomenclature committee:

“Clay minerals belong to the family of phyllosilicates and contain continuous two-dimensional tetrahedral sheets of composition T_2O_5 (T= Si, Al, Be,...) with tetrahedral being linked in the unit structure to octahedral sheets, or to groups of coordinated cations, or individual cations.”[15]

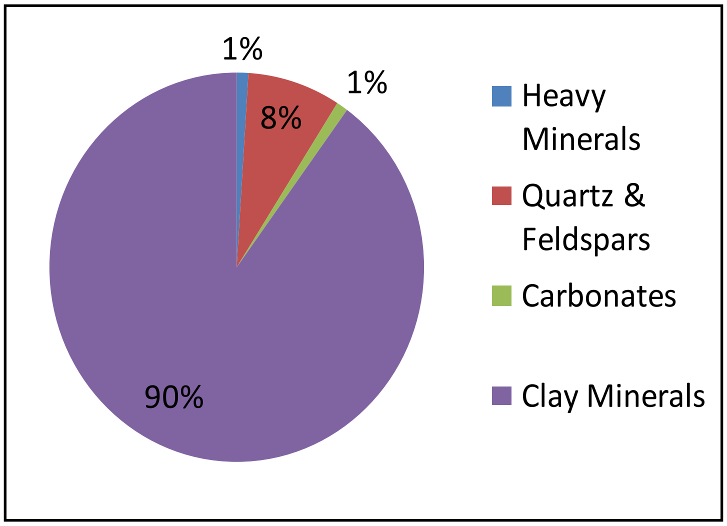


Figure 2-3 An estimate of composition of clay size fraction in oil sands [16]

Table 2-1 shows the clay composition of three different ores (W1, W2, W3) in tailings and froth studied by Adegoroye et al. [17]. CW1OF for example represents the clay in froth of ore W1. Kaolinite and illite are the major clay minerals. Presence of siderite is noticeable in poor processing ores, mostly in the froth rather than tailing streams [18]. There are also numerous studies focusing on solids characterizations in oil sands [19; 20; 21; 22; 23]. A fundamental understanding of solids in the froth is very important to improve the froth treatment process.

Table 2-1 Mineral phases present in the clay fraction of isolated solids [17]

Mineral phase	Samples (wt.% Rietveld)					
	CW1OF	CW1OT	CW2OF	CW2OT	CW3OF	CW3OT
Siderite	6	4	2	2	7	5
Kaolinite	53	48	52	49	54	48
Illite	20	22	25	18	19	10
Quartz	10	17	13	23	10	22
Zircon	<0.5	<0.5	<0.5	<0.5	<0.5	< 0.5
Microcline	4	4	3	4	3	7
Rutile	1	<0.5	<0.5	<0.5	<0.5	<0.5
Albite calcian	3	3	1	2	2	4
Pyrite	1	<0.5	1	1	3	1
Anatase	3	1	2	2	2	2
Calcite	0	0	0	0	0	0

2.3.1 Kaolinite

Kaolinite is a 1:1 type clay mineral which means that each layer contains one tetrahedral sheet and one octahedral sheet. As shown in Figure 2-4 the layers are bound by hydrogen bonding which makes them rigid and none-swelling in water. Because of 0.7 nm basal spacing, water and cations cannot occupy any space between the layers; therefore the external surface of kaolinite is same as its total surface area. Among all clay minerals, kaolinite is the most spherical clay mineral with the lowest aspect ratio [16]. Cation exchange capacity (CEC) is a measure of the ability of a clay mineral to adsorb exchangeable cations and it is very limited in the case of kaolinite [24]. For kaolinite there is limited isomorphic substitution on the surface, which leads to negligible negative charge on the basal clay surface [24]. Isomorphic substitution happens when Al^{3+} replaces Si^{4+} in the tetrahedral sheet or Mg^{2+} replaces Al^{3+} in the octahedral sheet. In every replacement a negative charge would appear on the clay surface since the cation is replaced by another cation that has lower positive charge. The charge resulting from isomorphic substitution is referred to as fixed or permanent charge [24].

Kaolinite particles could be charged on the edges, depending on pH due to change in O-H in different pH values. This is important since by controlling the pH it is possible to control dispersion or flocculation of the clay [25].

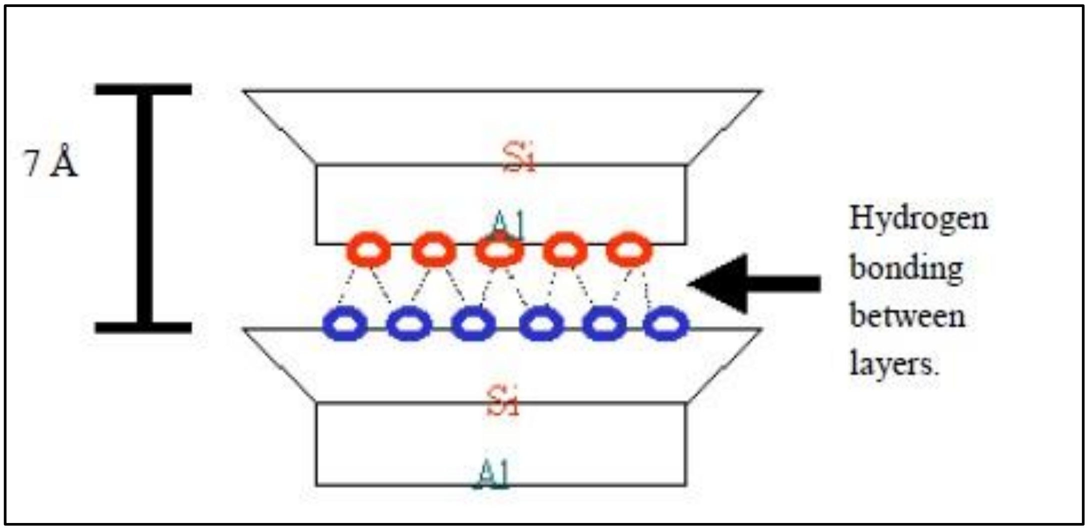


Figure 2-4 Kaolinite structure [26]

2.3.2 Illite

Illite is 2:1 type of clay with an octahedral sheet sandwiched between two tetrahedral sheets. About ¼ of Si is substituted by Al in the tetrahedral sheet which results in localized negative charge on the clay surface. Therefore clay particle tends to attract cations between its layers. There is high selectivity for potassium cation (K^+) in illite. In fact, K^+ fits very well in the hexagonal holes between tetrahedral oxygen groups. Due to ionic bond between negative charge of layers and cations, illite is none-expandable type of clay and the spacing between the layers is usually less than 1.0 nm [24]. It should be also mentioned that the CEC of illite is low just like kaolinite but its surface area is higher since illite is typically elongated or in the form of very thin sheets [16]. Figure 2-5 shows a schematic view of illite structure.

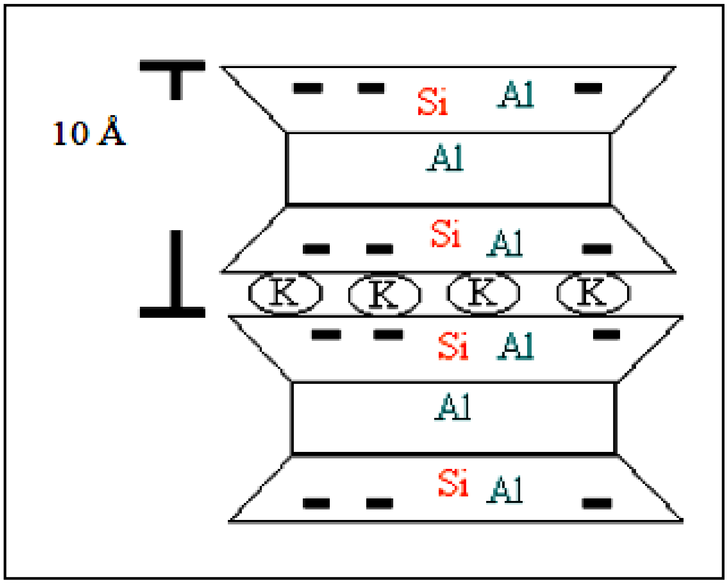


Figure 2-5 Illite structure [26]

2.3.3 Siderite

Siderite is another important component in the organic mineral complexation. It is usually found in weathered ores with high fines in the froth [27]. Siderite is the carbonate of calcite structure with formula of $FeCO_3$. In admixture with clays, it is referred to as clay ironstone. In the Sci-Tech Encyclopedia, siderite is defined as a mineral that is found in near surface ore deposits [28].

These three types of solids were used in this study as the major problematic model solids in the froth cleaning process.

2.4 Adsorption of organic compounds on solids

Hot water extraction process in oil sands is based on hydrophilicity of solids in the ore. Although it has been thought that there is a thin film of water around each solid particle in the ore matrix, completely hydrophilic solids do not exist in oil reservoirs, including Canada oil sands deposits [3; 29]. As reported in literature [27; 30; 31; 32; 33; 34; 35], there are inorganic solids that are covered by petroleum compounds referred to as organic rich solids (ORS). Presence of ORS could reduce the bitumen recovery in different ways. As shown in Figure 2-6, examples 1, 2 and 3 demonstrate buoyant bitumen drop. Because of adsorption of ORS particles on bitumen droplets, the density difference between oil and water is changed therefore the bitumen drops cannot float to the top. In Figure 2-6 ORS-BAGG refers to organic rich bi-wettable solid aggregates and ORS-HAGG refers to organic rich hydrophobic aggregates. Examples 4, 5, 6 and 7 represent the bitumen loss to the tailings because un-liberated bitumen remains trapped in some of ORS aggregates that are too heavy to float. They accumulate on top of the coarse tailings in a dark layer of organic rich material often reported in tailings from commercial operations. The major problem is accumulation of ORS at oil water interface, stabilizing both oil in water or water in oil emulsions.

Sparks et al. suggested that, the content of organic rich solids (ORS) in an ore appears to be a better indicator to evaluate the processability [29].

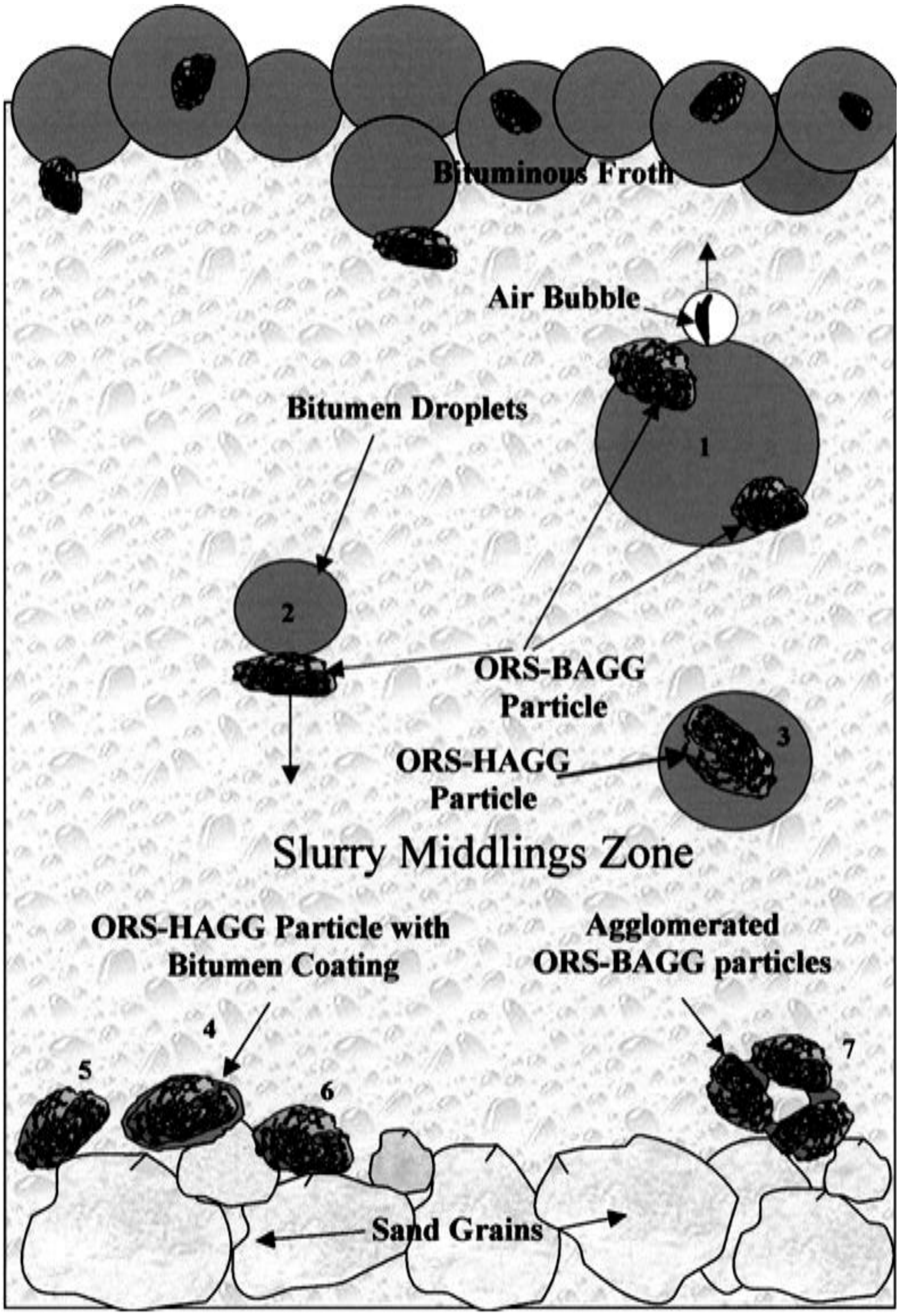


Figure 2-6 Conseptualisation of bitumen loss through interaction with ORS [29]

2.4.1 Adsorption of organic matter on solids

A simplified picture of organic adsorption on solid surface is shown in Figure 2-7. The particle surface is not fully covered by organics with areas free of contaminants. Humic matter covers large area of the particle surface since solids were deposited in soil and associate with plant humic matter before any contact with hydrocarbons in bitumen. Bitumen components, typically multi ring hydrocarbons, can adsorb on humic layers, or overlap on the particle surface [36].

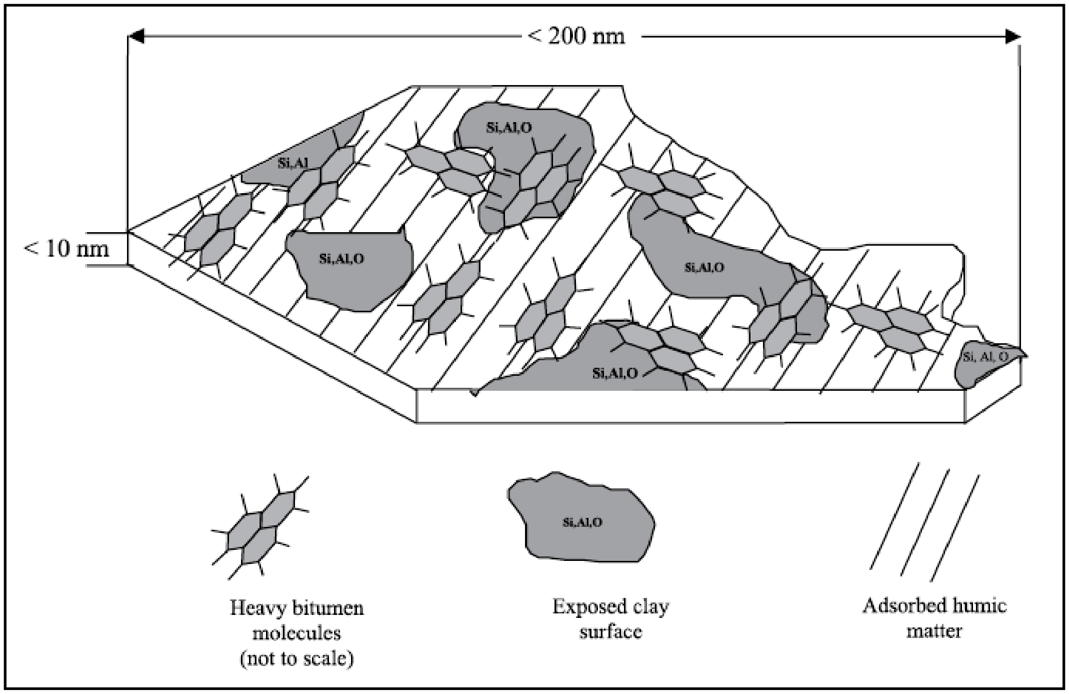


Figure 2-7 Particle coated with organics [36]

2.4.2 Characterization of organic rich solids

Several characterization techniques have been used to identify the common organic compounds that have an affinity to solid surfaces. X-ray photoelectron spectroscopy was commonly used to analyze the solids associated with organics. Detection of carbon and sulphur confirmed the presence of organic compounds [32; 34]. Si, Al and Fe were also found in the solids extracted from bitumen froth. In order to understand the structure of inorganic part of solids based on the detected elements, X-ray diffraction method was used. XRD patterns showed that most of the fine solids in oil sands are kaolinite, illite and crystalline iron oxides [18; 33]. Fourier transform infrared spectroscopy revealed the structure of organic compounds that tend to adsorb on solid surface. Resins and asphaltenes are important bitumen component that cover the solids [30; 35; 37; 38; 39; 40; 41; 42].

Hannisdal et al studied the adsorption of heavy crude oil components on different silica particles. It was illustrated that the most hydrophilic silica adsorbs more hydrocarbons and became hydrophobic because there was more free area (not coated by other chemicals) on the particles. FTIR study in the range of 2800 to 3000 cm^{-1} showed the adsorption of C-H carrying components on the silica particle, resulting in the modification of solid surfaces [43].

2.4.3 Major characteristics of organic rich solids in oil sands

Solid type: As mentioned in section 2.4.1 the major ORS found in oil sands are kaolinite, illite and iron oxides.

Water film around solid particles: Probably due to lack of thin water film around some particles, these solids adsorb compound similar to asphaltenes on their surfaces with irreversible adsorption. As a result, it is not possible to wash the surface organic contaminants by toluene. These compounds are referred to as toluene insoluble organic matters (TIOM) [29; 36].

Level of hydrophobicity: Tu et al proposed that the higher concentration of pentane insoluble organic matters leads to more hydrophobic clay surfaces [34].

Particle size: Although the size of the particle does not play an important role in contamination [14] with organics, the most problematic solids have the size less than 2 or 3 μm [44].

2.5 Role of organic rich solids in stabilization of emulsified water droplets in bitumen froth

Adsorption of organic matters on solid particles would change the surface properties so that the solids are no longer hydrophilic. They could be hydrophobic or bi-wettable. Therefore organic rich solids tend to form aggregates at oil water interface [45], which hinders separation due to the formation of stabilized water droplets in the diluted bitumen in froth treatment separation vessels.

As stated before, water droplets in the final product of froth treatment are stabilized by both heavy hydrocarbons and solids that form a rigid interfacial film around water droplets, preventing their coalescence. The solids at the interface are very small in size and partially covered by organics [44]. Since most of the particles in organic rich solids are clay minerals they are not spherical. In fact, they are more plate-like, often lying flat at the interface with a thickness less than 10 nm [46]. In a schematic representation system as shown in Figure 2-8, solid particles stabilize water droplets along with asphaltenes. If the solids are bi-wettable and sufficiently small they adsorb directly at the interface forming a rigid film around the droplets [47]. They may also adsorb on top of the asphaltene film, which restricts the drainage of oil between water droplets [46]. Some solid particles may form networks between water droplets [47] and prevent close contact and hence coalescence of water droplets, increasing emulsion viscosity [48].

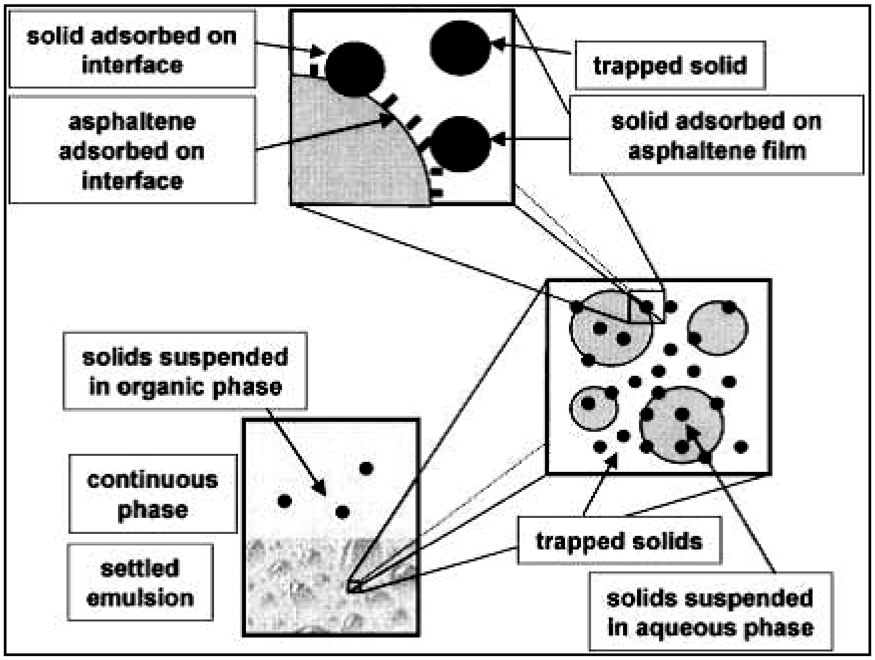


Figure 2-8 Role of solids in stablizing water droplets [46]

Sztukowski et al. extracted solids and asphaltenes from Syncrude coker-feed bitumen by addition of n-heptane to bitumen at the volume ratio of 40:1. Later they separated asphaltenes from solids by addition of toluene and centrifugation to remove solids. As shown in Figure 2-9, two series of emulsions were prepared and the amount of released water was measured to represent emulsion stability. In the presence of asphaltenes and solids the amounts of water released from the emulsion was less in comparison only asphaltenes. This observation means that emulsions in the former case are more stable than in the latter case. Therefore, it can be concluded that solids present in the emulsion would affect the stability of water droplets and prevent droplet coalescence [46].

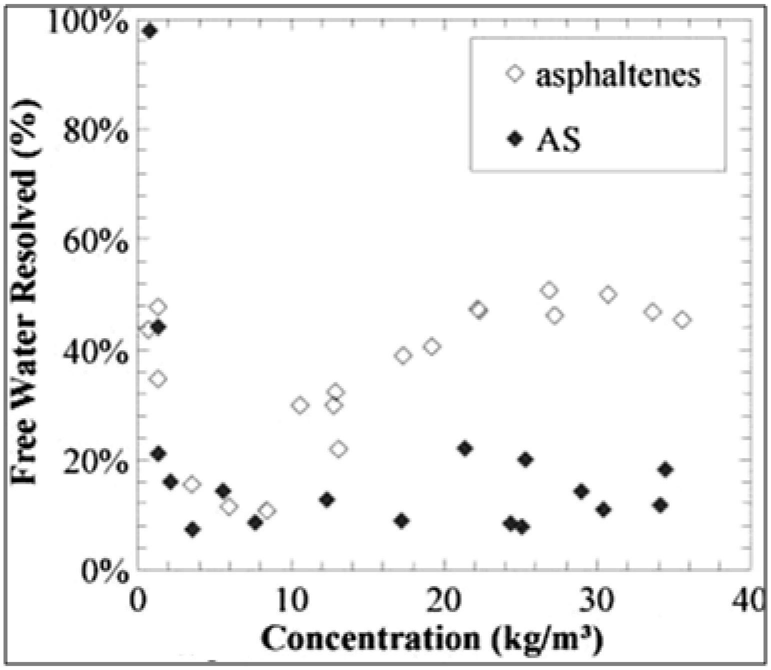


Figure 2-9 Stability of emulsions stablized by asphaltene and asphaltene-solids(AS) [46]

2.6 Emulsion stabilized by solid particles

The fact that fines can stabilize emulsions has been known since the early 1900's when Pickering noted the importance of solids wettability on emulsions formation [49]. The term Pickering emulsion is now commonly used to describe solid stabilized emulsions. Four years earlier in a paper cited by Pickering [50], the formation of membrane of solid particles stabilizing air bubbles in water was described [51]. Over the last 100 years solids stabilized emulsions have been studied in great detail [12; 52; 53].

Thermodynamically, the energy of detachment of a particle at an oil-water interface depends on many factors. Assuming that the particle is small enough to neglect gravity, the energy required to remove the spherical particles from the interface is given by:

$$\boldsymbol{E = \pi r^2 \gamma_{ow} (1 \pm \cos\theta)^2} \qquad \textbf{(1)}$$

The sign inside the bracket is positive for removal into the oil phase and is negative for removal into the aqueous phase [51].

As shown in equation (1) interfacial tension (γ_{ow}), particle size (r) and particle contact angle (θ) are important factors in solid stabilized emulsions. In addition there many other factors that contributes to the stability of a Pickering emulsion.

2.6.1 Effect of hydrophobicity of solids

To evaluate the location of solid particles at oil-water interface, contact angle as a relevant parameter was introduced. Hydrophilic particles have a contact angle less than 90° and hydrophobic particles have a contact angle greater than 90°. Briggs observed hydrophilic silica particles formed oil-in-water emulsions, while carbon black (hydrophobic) stabilized water-in-oil emulsions [54]. Such formations relate to the most energetically favorable state. This has been observed multiple times where water-wet particles stabilize oil-in-water and oil-wet particles stabilize water-in-oil emulsions [55; 56] as shown in Figure 2-10.

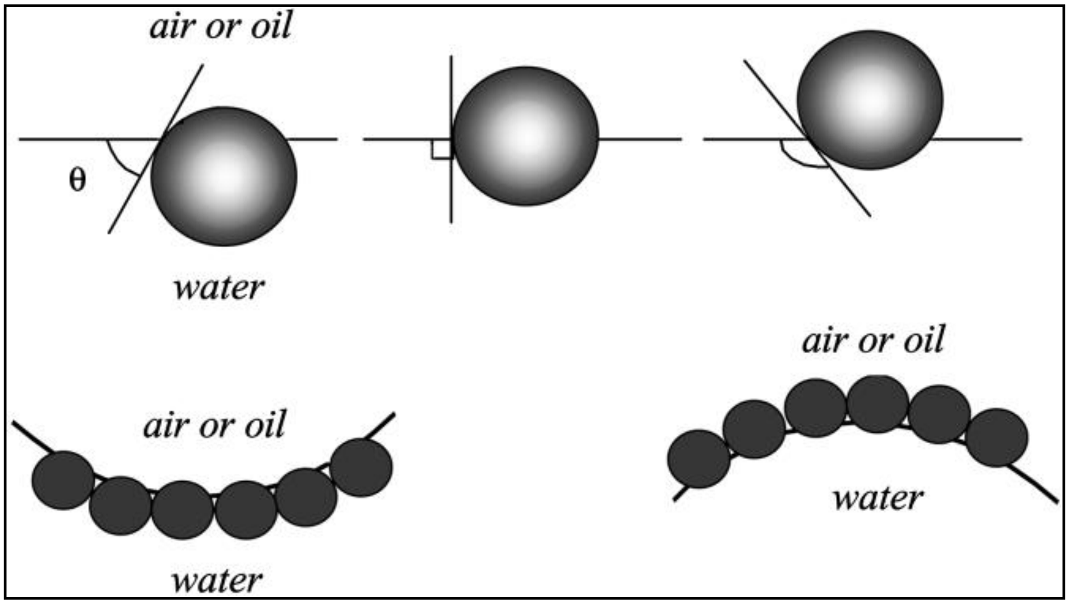


Figure 2-10 Position of spherical particle at oil water interface, outlining the importance of partcle wettablity in stabilizing emulsions [48]

Yan et al. used treated silica particles to study the effect of contact angle on emulsion stability [44]. In their work silanols on silica surface were replaced by silane or siloxane hydrophobizing agent in a continuous gas/solids fluidization process, resulting in silica particles of six different contact angles. Particles were used in a system of 1:1 toluene-water volumetric ratio to produce emulsions; results are shown in Figure 2-11. Hydrophilic silica samples did not produce stable emulsions. As the hydrophobicity increased higher volume of emulsion began to form. However in samples #5 and #6 silica particles are too hydrophobic to stabilize all of the water in to the emulsion.

In order to stabilize an emulsion the particles should be able to position at the oil-water interface. This is possible when the particles are bi-wettable or partially hydrophobic. If the particles are too hydrophilic most of the particles reside in water and the efficiency of attachment is low hence particles can readily detach from the interface. Such an interface is not sufficient to provide a barrier to prevent droplet coalescence [48]. The same situation is observed with particles are extremely hydrophobic [53]. Particles of an intermediate hydrophobicity are most effective in stabilizing an emulsion.

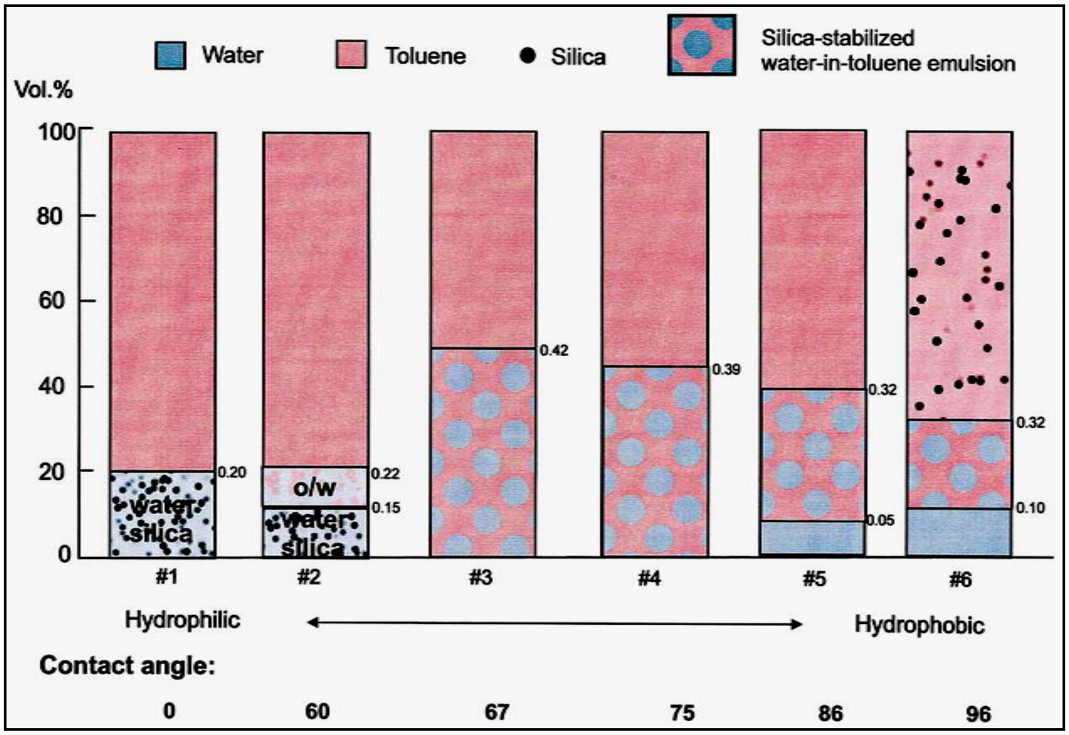


Figure 2-11 Water toluene emulsions stabilized by silica particles with different contact angles [44]

2.6.2 Effect of particle size

Generally, when there are fines positioned at the interface, emulsion is observed to be stable [57]. Binks et al. investigated the effect of particle size on stability of emulsions [58]. The authors found that an increase in particle diameter increased the average droplet size (solid circles in Figure 2-12) of water-in-oil (w/o) emulsions. The median droplets size (empty circles in Figure 2-12) showed little variation. Thus, it was concluded that population of larger droplets increased by using larger particles. They also mentioned that emulsion stability decreased due to the sedimentation of larger droplets.

Not much research has been carried out on the effect of particle size distribution on emulsion formation. Only Sethumadhavan et al [59] proposed that solid particles with narrow size distribution would better stabilize foams. Extending this theory to emulsions, monodisperse particles would form more stable emulsions [46].

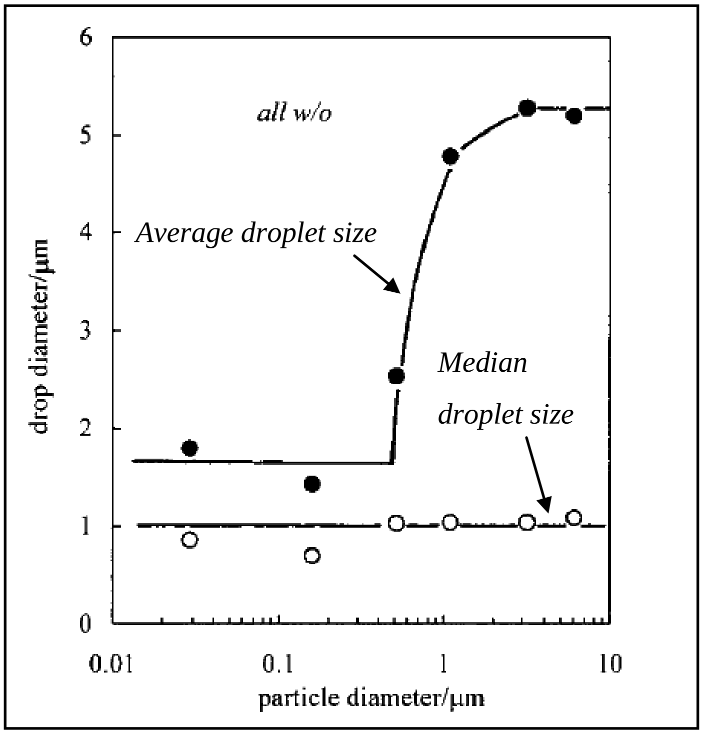


Figure 2-12 Effect of particle size on water droplet size [58]

2.6.3 Effect of particle concentration

From several studies, an increase in solids concentration was found to result in emulsions of higher stability [12; 47; 48].

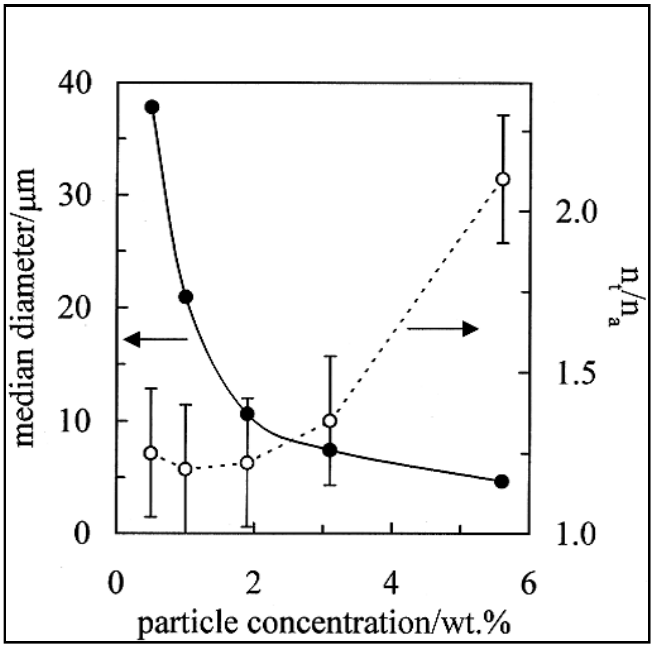


Figure 2-13 Median drop diameter as a function of particle concentration [48]

In Figure 2-13, the change in median drop diameter as a function of hydrophilic silica concentration is illustrated. Droplet diameter decreased by the addition of solid particles which increased the emulsion stability [48]. Also, it was assumed that all particles are adsorbed in the form of hexagonal monolayer. By knowing the drop size distribution, the ratio of total number of particles to the adsorb particles, n_t/n_a could be calculated. As shown in Figure 2-13, at about 3 wt% particle concentration, n_t/n_a started to increase, indicating saturation coverage of the droplet surface by silica particles at this solid concentration. The excess remaining silica caused gelation [60] in the continuous phase, which explains the increase in emulsion viscosity by the addition of particles [61].

2.6.4 Effect of oil phase

Where solids are the major emulsion stabilizers, the interaction of solids with both liquids and also at the interface defines the contact angle of solids, which is the key factor in the stabilization of droplets. Considering that the contact angle is altered in different oil phases, the nature of oil phase can ultimately determine the type and properties of the emulsion. Binks and Lumsdon measured the contact angle of water drops on hydrophobized glass in different oil phases. They proposed that the contact angle is higher when the oil phase is more polar and the surface tension is relatively low. In the case of none-polar oil-water interface, the particle surface looks more hydrophilic and the contact angle value is lower [62]. In another theoretical work, Binks and Clint compared the calculated and experimental value of contact angles for seven different solid surfaces in different oil phases. This study supported the assumption that increasing hydrophobicity requires oils of higher polarity.

In the case of bitumen, the oil phase is not only polar but also contains natural surfactants. Adding surfactants to a system which includes solid particles was found to decrease van der Waals attraction due to an increase in average inter particle distance in the presence of surfactants [63]. Therefore, it can be concluded that the presence of bitumen as a part of oil phase in an emulsion results in a change surface energy of solids.

2.6.5 Effect of aqueous phase

Addition of salts to the water would result in aggregation of particles. To form a stable emulsion, particles should be either dispersed or weakly flocculated [48]. In the case of silica increase in pH resulted in a higher negative charge on the particle surface and better dispersion, leading to formation of more stable emulsions; just like surfactants in the oil phase as mentioned in section 2.6.4 [62]. In the case of bitumen as an oil phase, increase in pH reduces interfacial tension between oil and water, because of higher concentration of surfactants in the system.[53]

2.6.6 Effect of volume fraction of water

Binks et al. performed series of comprehensive experiments on solids stabilized emulsions [48]. They synthesised a number of fumed silica batches of same size and distribution. Each batch reacted with dichloro dimethylsilane in the vapour phase under a controlled condition. As a result, silica samples with different hydrophobicities were prepared. The percentage of SiOH on the surface of particles represented their hydrophobicity. For example, particles of 100% silanol group on the surface were very hydrophilic and those with 14% silanol group were very hydrophobic.

The silica sample with 57% SiOH was used in studying toluene-water emulsions at different water fractions ϕ_w. As shown in Figure 2-14, six emulsions were prepared at $\phi_w = 0.4, 0.6, 0.65, 0.7, 0.8, 0.9$ either by sequentially water addition (open points) or toluene addition (filled points) [61].

The type of emulsions was determined through conductivity measurement. Oil continuous resulted in a low conductivity and water continuous a high conductivity. Therefore, at around $\phi_w = 0.65$ the emulsion converted from water-in-oil to oil-in-water (ϕ_w^{inv}) as indicated by a sharp change in conductivity, shown in Figure 2-14b. All the emulsions were stable without noticeable coalescence. However the drop diameter was very different in w/o (1 µm) and o/w (100 µm) emulsions due to hydrophobic nature of the silica sample used in this experiment [48].

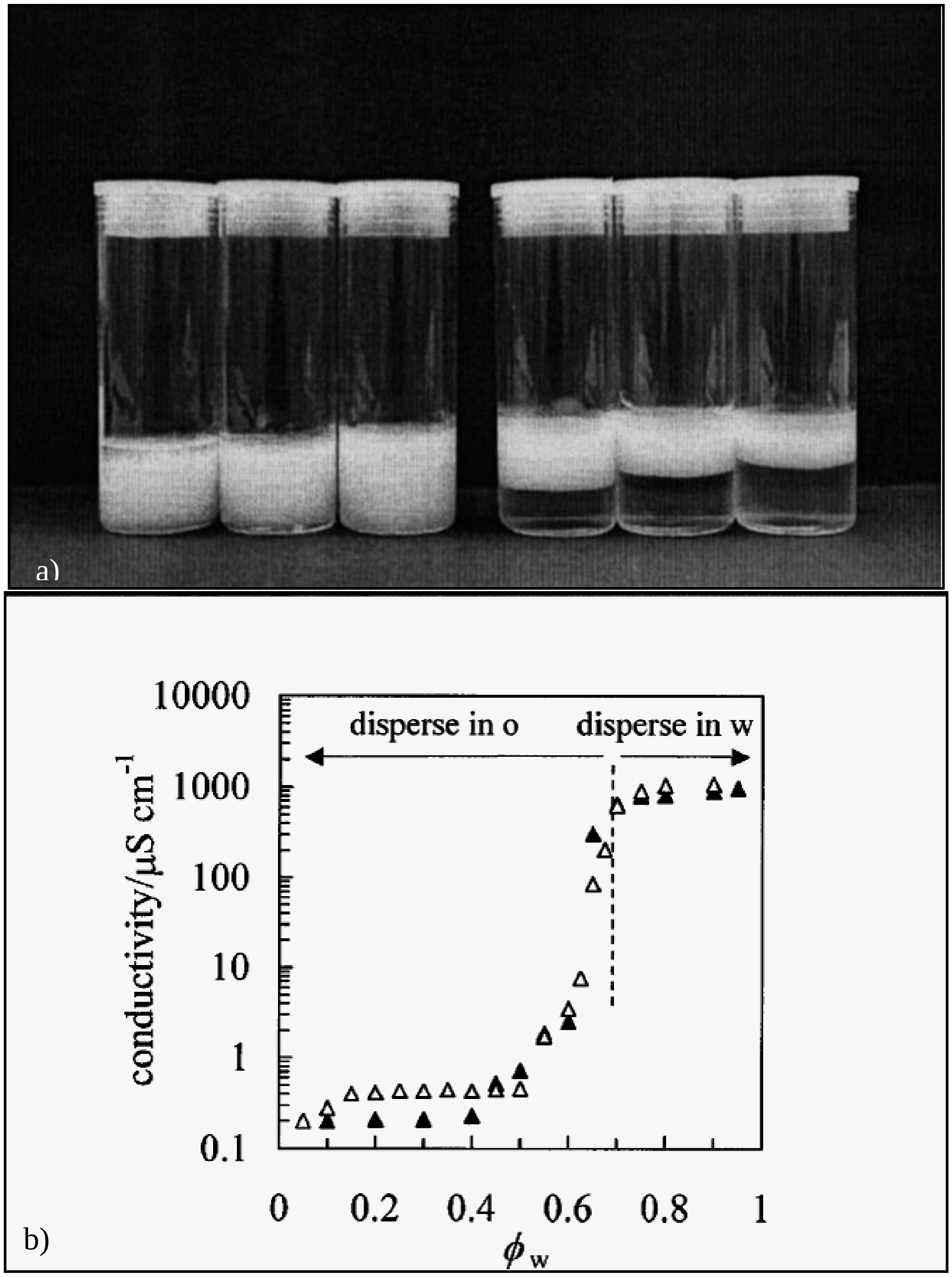


Figure 2-14 a) Appearance of emulsions b) Conductivity of emulsions [61]

Same experiments for other silica samples with different hydrophobicities showed that as the particles became more hydrophobic the ϕ_w^{inv} increased from 0.35 to 0.8 [60].

3 Experimental

3.1 Materials

Coker-feed bitumen from Syncrude Canada was used in all experiments. Clays including kaolinite, illite and siderite were purchased from WARD'S Natural Science, and silica was purchased from Fiber Optic Centre. Acetone and HPLC grade toluene were bought from Fisher Scientific. Deionised water used for emulsion preparation had a conductivity of 15 MΩcm.

3.2 Equipment

3.2.1 Set up for grinding

Since the purchased clay minerals were significantly larger than those encountered in froth treatment, kaolinite, illite and siderite, were ground using zirconium oxide balls. Three different size of balls (6mm, 4.7mm and 2.8-3.3mm in diameter), were bought from Union Process. A mixture of grinding balls containing 30 wt% 6 mm, 40 wt% 4.7 mm and 30 wt% 2.8-3.3 mm balls was prepared and used in the grinding, (Figure 3-1a). Using the grinding ball of different sizes, would enhance the efficiency of grinding process. About 20 g of water and 20 g of clay were added to a 50 mL jar with the same volume of grinding ball mixture added on the top of the clays. A ceramic impeller as shown in Figure 3-1b was connected to a mixing rotor. The level of the rotor and the impeller in the jar was adjusted to be a few millimeters up from the bottom of the jar. As the impeller started to rotate 1000 rpm the grinding process started. Sampling for particle size measurement was performed regularly, until no visible variation was measured. The grinding process took 40 hours for kaolinite and 32 hours for illite and siderite.

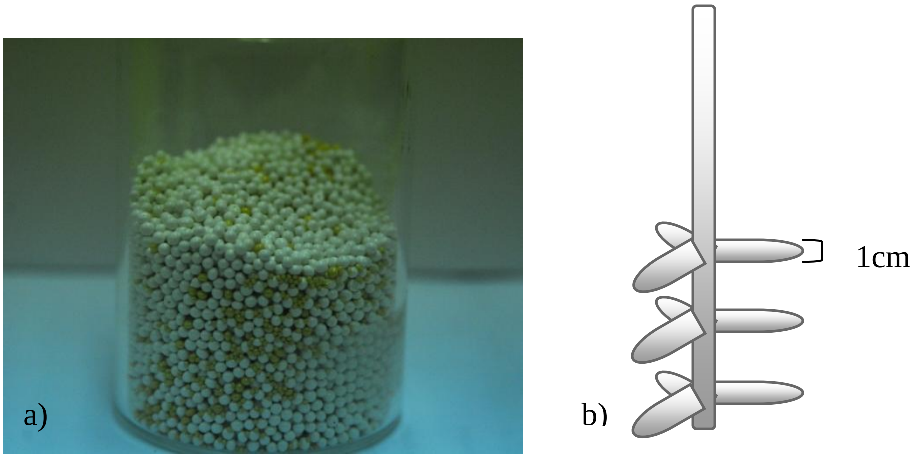


Figure 3-1 a) Grinding ball mixture; b) Ceramic stirrer

3.2.2 Particle size analyzer

To measure particle size distribution (PSD) of model minerals before and after grinding, 0.1 g of sample and about 15 mL DI water were added to a 20 mL vial and sonicated for at least 20 minutes to disperse particles. PSD was measured using a Malvern Mastersizer 2000 particle analyzer (Malvern instruments Ltd., UK). The measurement of this instrument is based on laser ensemble light scattering. The system has a chamber in which water is kept agitated during the measurement. A few drops of dispersed sample, right after sonication, were added to the chamber. The laser beam from the analyzer passes through the sample and scatters. The intensity and angle of the scattered light depend on the particle size in the suspension. The PSD as well as D10, D50 and D90, between 0.1 micron and 1000 micron, were calculated based on Mie scattering model [64].

3.2.3 Surface area analyzer

Quantachrome Autosorb 1MP measures surface area by calculating the amount of gas adsorbed or desorbed from a solid surface at a given temperature measuring pressure changes occurring within a constant volume. This instrument is equipped with two ports for sample outgassing and one port for sample measurement. N_2 is the standard probe molecule used, but Ar and Kr can also be used.

Samples were first prepared by heating while gas was simultaneously flowing over the sample to remove the liberated impurities. Outgassing time might vary from one sample to another. Samples were then cooled by liquid nitrogen and measurements started. As nitrogen gas was passed over the sample a monolayer of nitrogen molecules was adsorbed onto the surface of the particles. The relative pressure range the instrument can detect is from 0.001 bar to slightly less than 1.0 bar. The volume-pressure isotherm data can be readily converted to surface area using BET method (Brunauer, Emmett and Teller) [65].

3.2.4 X-ray diffractometer (XRD)

X-ray diffraction method is a rapid none-destructive technique to identify clay minerals. This technique is based on Bragg's equation:

$$\mathbf{n\lambda = 2d\sin\theta} \qquad \textbf{(2)}$$

where d is distance between atomic plates, n, an integer (1,2,...), λ, the wave length and θ, angle of incidence of X-ray beam on the atomic plate.

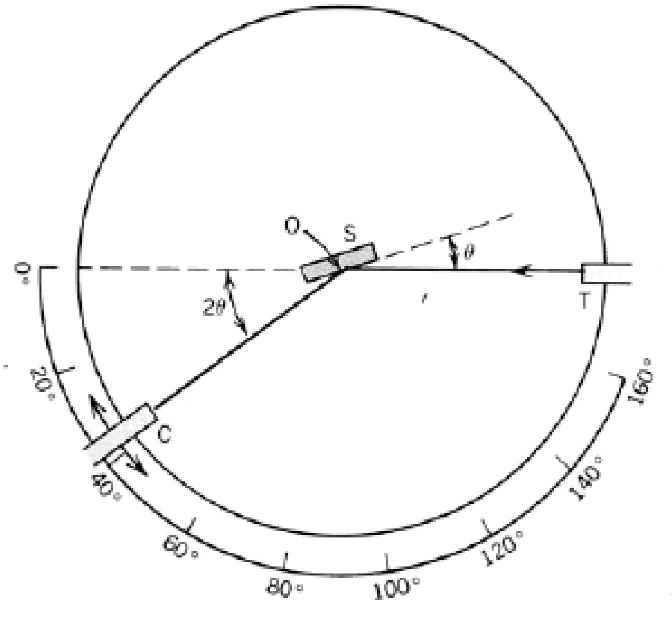


Figure 3-2 Schematic view of XRD [66]

In Figure 3-2 it is assumed that a parallel and monochromic X-ray beam, of wave length λ is incident on sample at an angle θ; 2dsinθ is the path length difference between two incident X-ray beams. They take a parallel path because they are reflected off an atomic plane. The path length is equal to an integer value of λ so that reinforced diffracted beam is produced. By varying θ, the Bragg's equation condition is satisfied for different d-spacing in materials. Plotting intensity of diffracted beam versus angle of incidence (θ) produces a pattern, which is a characteristic of the sample.

X-ray tube is the vacuum tube that produces X-rays, which can be a fixed or rotating tube. Instrument used in this experiment is RIGAKU rotating anode XRD system. To prepare samples, a layer of vaseline on a 1/2″×1/2″ glass slide 3″×1″ was smeared. The sample powder was then added on the top of vaseline and pressed to make it stick to the glass slide. The glass slide was then inserted into the horizontal goniometer. The sample was scanned by the incident X-ray beam from 10 degrees to 110 degrees at a scan rate of 2 degrees per minute.

3.2.5 Fourier transform infrared spectrometer (FTIR)

BioRad FTS6000 was used to obtain infrared spectra of mineral samples prepared in this study. This instrument is capable of recording infrared spectra of samples for a wavenumber in a range of 11000 to 400 cm^{-1}. Figure 3-3 shows working principals of FTIR.

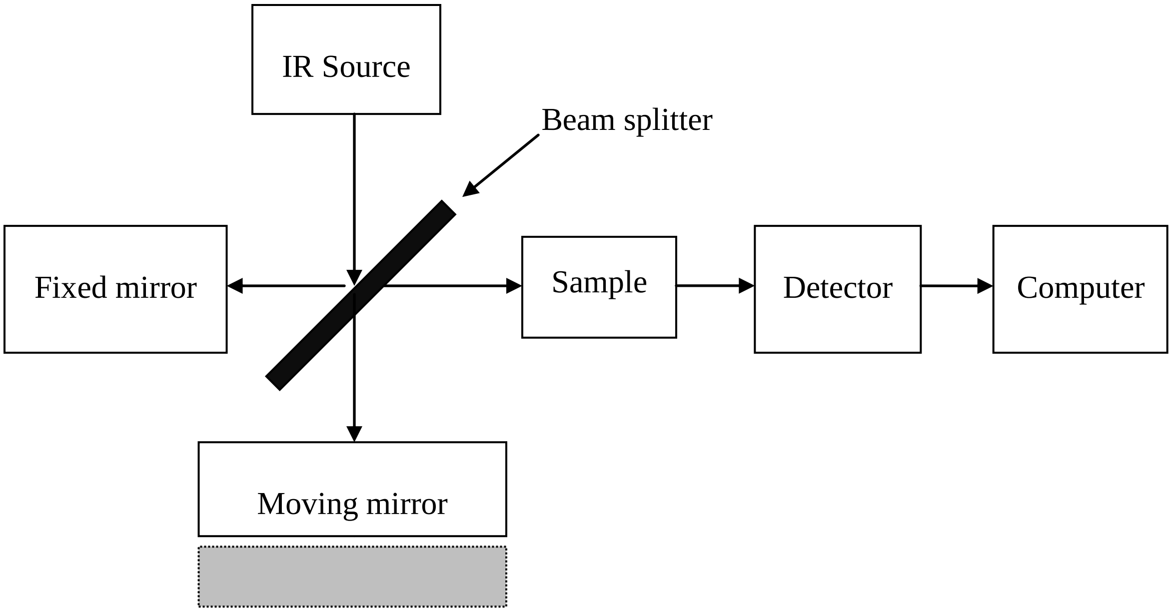


Figure 3-3 FTIR block diagram

As shown in Figure 3-3, light from an IR source is directed to a beam splitter, BS. Beam splitter reflects half of the light to the fixed mirror and half of the light to a moving mirror. Beams are returned to the BS after they passed certain distances which in the case of moving mirror is variable. Then the recombined beam at BS passes through the sample. The radiation coming out of sample compartment is converted to an electric signal at the detector. The output after processing is read out in a plot in the form of percent transmission versus wave number [67].

To use FTIR, the detector of the instrument should be cooled down by liquid nitrogen 20 minutes prior to measurements. KBr was used as a reference to take background spectrum. To prepare sample for FTIR analysis, 0.1 g of KBr was mixed and ground with 1-5 mg of mineral sample in 35 mL mortar and pestle with a hand. The ground sample was transferred to the sample holder and analyzed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

3.2.6 Drop shape analyzer (DSA)

Contact angle measurements were carried out with a Drop Shape Analyzer (KRÜSS inc., Germany). The instrument works with both automatic and manual adjustment to control droplet volume. The contact angle from 0 to 180 degree can be measured with 0.1 degree of accuracy. As shown in Figure 3-4 the set up includes an adjustable platform and a CCD camera which captures the shape of the droplet and transfers it to videos for later analysis using the software equipped with the instrument. Specifically, the software can determine the droplet and the baseline automatically. Then by fitting a mathematical expression and calculating the tangent at liquid-solid-vapor (LSV) interface, the contact angle can be obtained.

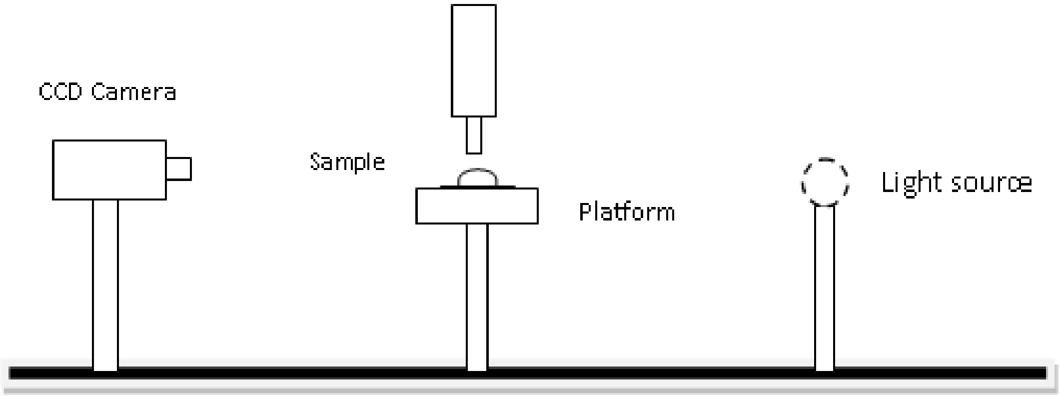


Figure 3-4 Schematic view of a drop shape analyzer

To prepare the sample for contact angle measurements, 0.2 g of minerals were first dispersed in 20 mL toluene for at least 30 minutes. A clean silica wafer was placed on a spin coater. A vacuum was applied to hold the silica wafer on its place while the spin coater is running. While the wafer was spinning at 6000 rpm, 20 droplets of dispersed sample were added on the silica wafer very carefully. After the addition of the sample, the spin coater continued to run at the same speed until complete evaporation of toluene. The sample was then transferred to DSA platform using tweezers, with the effort to avoid touching the layer formed on the top of the wafer.

3.2.7 X-ray photoelectron spectroscopy (XPS)

In the X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), the sample is irradiated with soft X-ray photons (1-2 keV). The X-ray would excite the inner electrons of sample atoms and cause direct emission of photoelectrons. The emitted photoelectrons are characteristic of the sample. Therefore, measurements of the energy spectrum (number of count vs. kinetic/binding energy) provide valuable information on the thin layer (about 20nm) of atoms on the surface of sample, depending on the material studied. Peak position and peak area are used to evaluate the composition in that layer. This technique is valuable when the analysis of contamination on the surface of materials is the target of study.

The XPS measurements were performed on AXIS 165 spectrometer (Kratos Analytical) at the Alberta Centre for Surface Engineering and Science (ACSES). The base pressure in the analytical chamber was lower than 3 x 10 Pa. Monochromatic Al Kα source ($h\nu$ = 1486.6 eV) was used at a power of 210 W. The surface area of analysis was 400 x 700 um. The resolution of the instrument is 0.55 eV for Ag 3d and 0.70 eV for Au 4f peaks [68].

The survey scans were collected for binding energy spanning from 1100 to 0 eV with an analyzer pass energy of 160 eV and a step of 0.4 eV. Electron flooding was used to compensate sample charging. Vision-2 instrument software was applied to processing. Compositions were calculated from the survey spectra using the major peaks and sensitivity factors of the elements provided by the database.

3.2.8 Scanning electron microscope (SEM)

To investigate the morphology of solid particles, a scanning electron microscope was used. The solid powder was placed on top of carbon shielded stubs and then coated with gold using Xenosput XE200 or Nanotek SEM prep 2 sputter coaters before the measurement. The SEM used in this study is a Zeiss EVO MA 15. Our

JEOL (Field Emission Scanning Electron Microscope) equipped with a Bruker Silicon Drift Detector for Energy Dispersive X-Ray analysis/ mapping with a LaB6 crystal source that provides images with 5 nm resolution. The images were obtained at an accelerating voltage of 20 keV, working distance of 17 mm and magnifications of 20x to 100 000x. The elemental analysis is assumed to be semi-quantitative as the x-ray take off angle was not constant due to the roughness of the samples [69].

3.2.9 Homogenizer

To prepare emulsions, a PowerGen 125 mechanical Homogenizer was used. A schematic of the instrument is shown in Figure 3-5. This device includes a tube and collar assembly that is referred to as stator parts because they do not move. Inside the tube there is a rotor knife connected to the motor shaft which is coupled directly to the drive motor and can spins at up to 30000 rpm. As the knife spins within the stator, it creates a pumping action which pulls liquid into the probe and forces liquid out through windows, inducing a shear action. The speed differential between the rapidly moving liquid being pumped by rotary knife and the relative stationary liquid (rest of the sample), creates a second force, called cavitation. Constant circulation continues to impact these forces on the sample; leading to continuous shear of the sample. As a result, the mechanical homogenizer is more efficient than ultra sonic homogenizers.

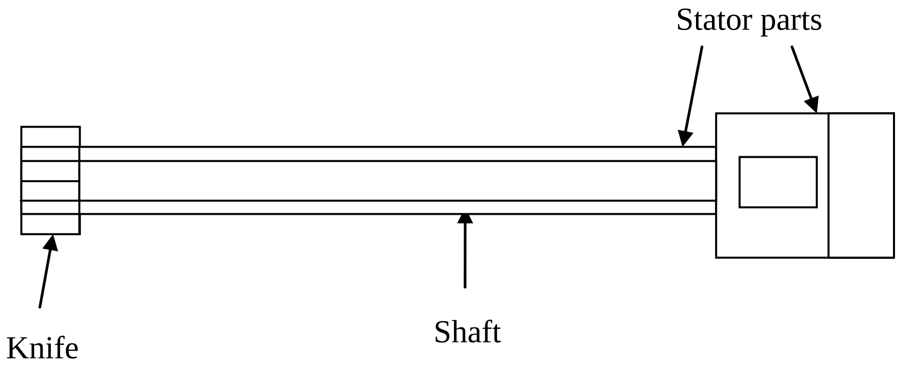


Figure 3-5 Schematic view of Homogenizer

3.2.10 Karl fisher titrator

Cou-10 Karl fisher titrator was used to measure water content in diluted bitumen. The water present in the sample is coulometrically titrated to a predefine end point. Stoichiometrically, 1 mole of water will react with 1 mole iodine. Therefore 1 milligram of water is equivalent to 10.71 coulombs of electricity. Therefore the instrument can determine water content of the sample by measuring the amount of electrolysis current necessary to produce the required iodine [70].

$I_2 + SO_2 + 3C_5H_5N + H_2O \rightarrow 2C_5H_5NHI + C_5H_5NOSO_2$

$C_5H_5NOSO_2 + CH_3OH \rightarrow C_5H_5NHSO_4CH_3$

$2I^- - 2e \rightarrow I_2$

3.2.11 Optical microscope

Water droplet size was determined optically by an Axioskop 40 Pol microscope, shown in Figure 3-6. With capacity of transmitted-light/ reflective-light in this microscope it is possible to observe the transparent or very dark sample. Also binocular phototubes and adaptor enable one microscope camera and one reflex camera to be attached for recording micrographs.

To measure water droplet size in each test, at least 10 images were taken. With the software it is possible to measure the droplet diameters. The d_{50} of at least 50 water droplets analyzed was reported as the droplet diameter.

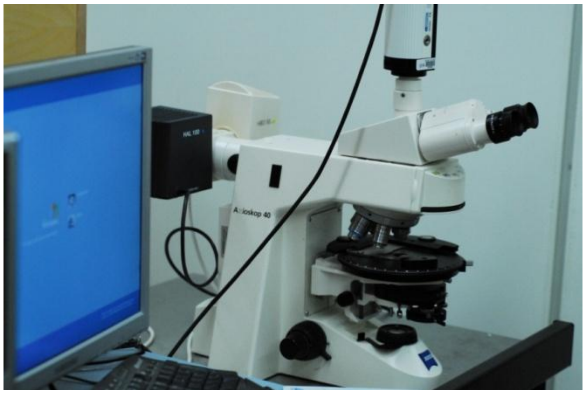


Figure 3-6 Picture of microscope

3.2.12 Micropipette test

Micropipette technique allows the study of interactions between individual water droplets in the emulsion using small suction pipettes. Brosilicate glass tubes with 1mm outer diameter and 0.75 mm inner diameter (Fredrich & Dimmock, USA;SYN-BCT-75136) were used. The tubes were stretched axially using an extruder (David Kopf instruments, Tujunga, CA: model 730) to produce tapered tubes. These tubes were truncated with an in-house built forging device, resulting in hollow pipette tips of 5 to 10 micron inner diameter [71].

To perform the test the emulsion was first diluted by toluene. Droplet contact test was performed to evaluate the probability of coalescence between two water droplets in contact. In details, two micron sized droplets were held in contact with each other by two micropipettes for 20 seconds and then were pulled away from each other, as shown in Figure 3-7. During the contact, some pressure was applied to make the droplets pressed against each other. As a result the water droplets might or might not coalesce. The probability of coalescence was determined based on 30 contact events of different water droplets for each sample.

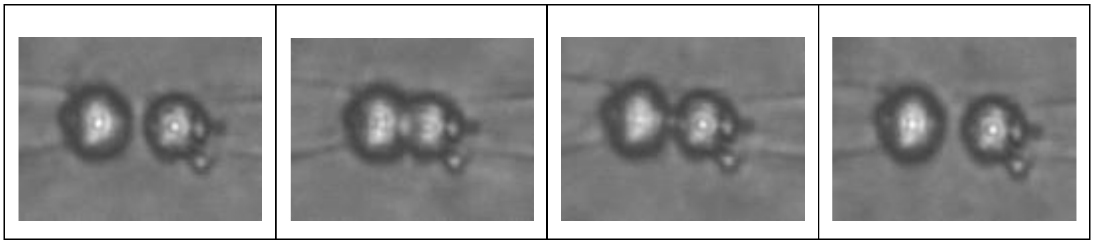


Figure 3-7 Sequential visualization of micropipette technique

4 Adsorption of bitumen components on particles

Wettability of solids may alter due to exposure of solid surface to organics as in oil sands processing where solids particles are in contact with bitumen. To understand a complex system such as bitumen forth, it is better to start with a model system since it is easier to perform a mechanistic study and identify key factors. Four types of solids encountered in bitumen froth treatment were used in this study. They are kaolinite, Illite, siderite and silica.

In this chapter the tendency of solids to adsorb bitumen components on their based on their surface properties and moisture content was investigated. In the first part, samples were prepared and treated by diluted bitumen. In the second part, the effect of solid type, solid size, moisture content and bitumen concentration on adsorption of bitumen components on solid surfaces was studied. The results showed that all types of dry solids adsorb organic compounds in bitumen.

It should be also noted that in a previous study [72], Yang discussed the wettability alteration/contamination of four minerals in different solvents in a model system with low bitumen content. He used the same model minerals: kaolinite, illite, siderite and silica in wet and dry conditions. He observed that the dry siderite had the most change in contact angle. However, in this study the minerals were ground to smaller sizes and the bitumen content is closer to the naphthenic froth treatment.

4.1 Sample preparation and treatment

4.1.1 Grinding solid samples to similar sizes

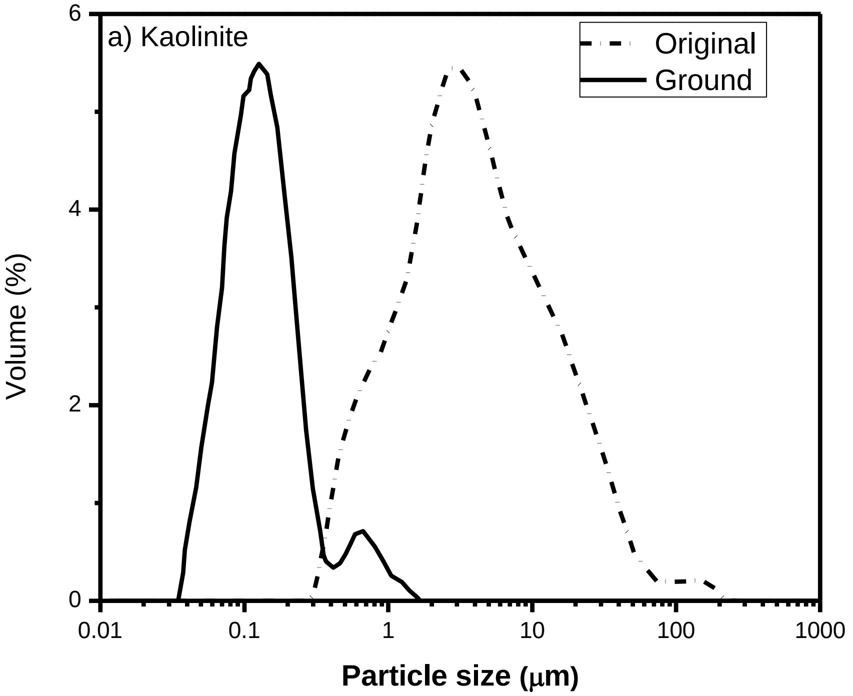
Four types of solids were used to model the solid particles in froth treatment process. The original kaolinite, illite, siderite and silica that were bought, had different sizes. Table 4-1 below shows the d_{50} of solids measured by particle size analyzer. The d_{50} is defined as the size in micron where half of the population has the value below this diameter on the volume distribution diagram. It is also called median for particle size distribution.

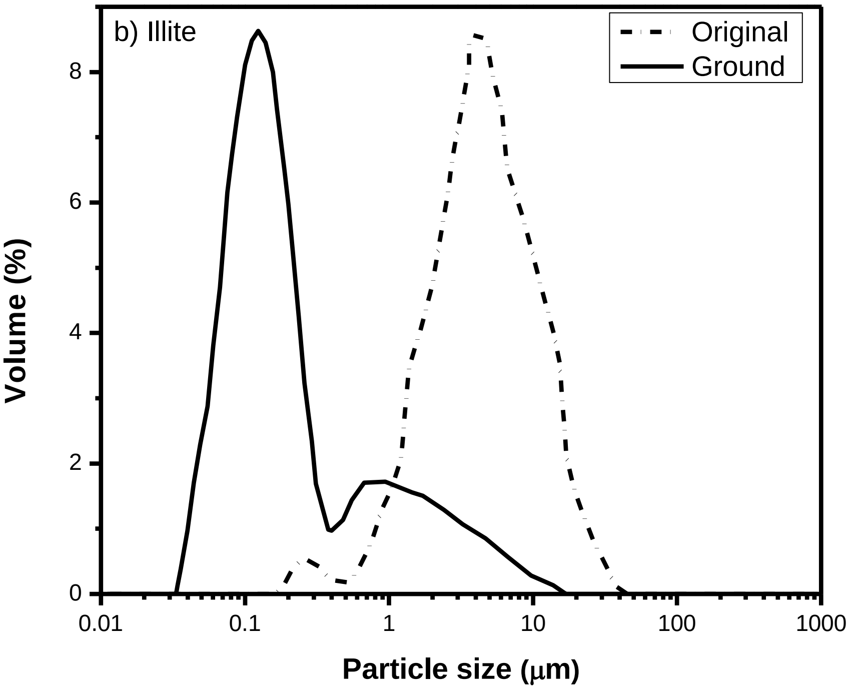
Table 4-1 Original size of model solid samples

Solid type	Original d_{50} (µm)
Kaolinite	4.58
Illite	3.78
Silica	0.25
Siderite	Chunks

To perform a systematic study on all samples, the solids should be of similar size range. For example, the d_{50} measured for silica is about 250 nm which is significantly smaller than 18 times larger kaolinite particles or chunks of siderite. Also it has been reported that problematic solids in real froth are very small in size (about 0.5 µm) known as ultrafines [23]. Therefore kaolinite, illite and siderite were ground to achieve a similar size range to that of real froth solids and silica.

To achieve a higher grinding efficiency three different sizes of zirconium oxide grinding balls were used. Each batch contained only less than 15 grams of solids. Figure 4-1 shows the particle size distribution for three solids. In this figure, part a and b show the kaolinite and illite size distribution before and after grinding. There are complete shifts in peaks in both PSD diagrams, which indicate a significant reduction in particle size for both samples.


a) Kaolinite
Original
Ground
Volume (%)
6
4
2
0
0.01
0.1
1
10
100
1000
Particle size (μm)


b) Illite
Original
Ground
Volume (%)
8
6
4
2
0
0.01
0.1
1
10
100
1000
Particle size (μm)

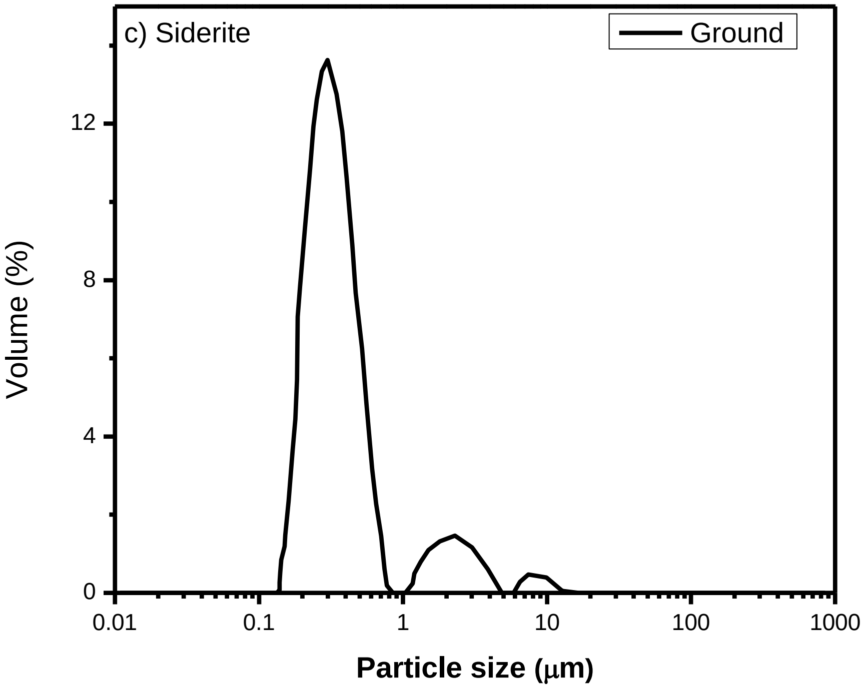


Figure 4-1 Particle size distribution for a) kaolinite; b) illite and c) siderite

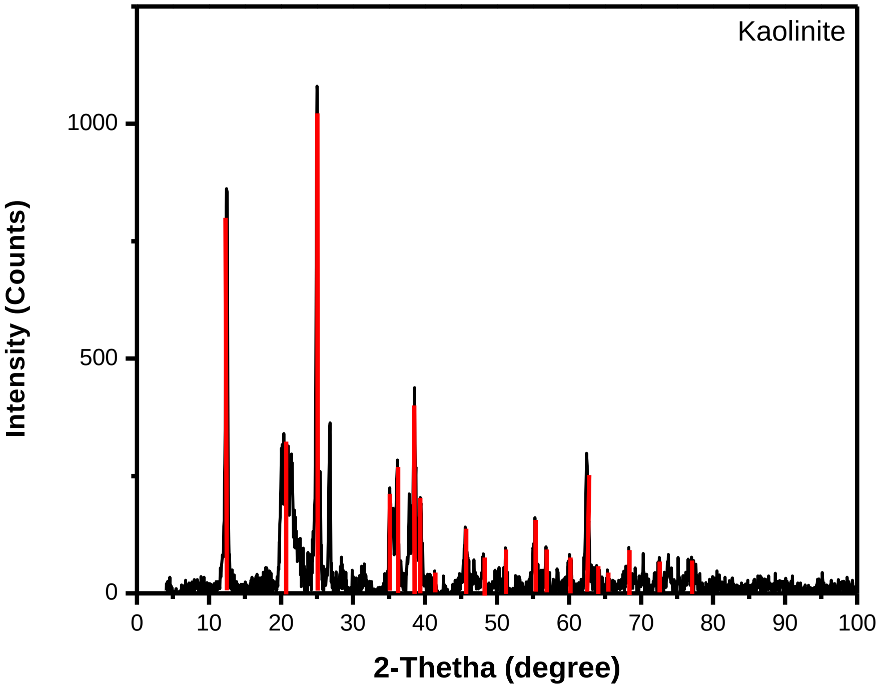
In the case of siderite, mortar and pestle were first used to break the chunks of siderite to smaller size and then the ball mill grinding was performed. The final d_{50} for all types of solids are shown in Table 4-2. All samples have median size below 0.5 μm. After the grinding the special surface area has been measure for kaolinite sample before and after the grinding. The surface area for original sample was 10.8 m^2/g and it decreased by grinding to 78 m^2/g for ground kaolinite.

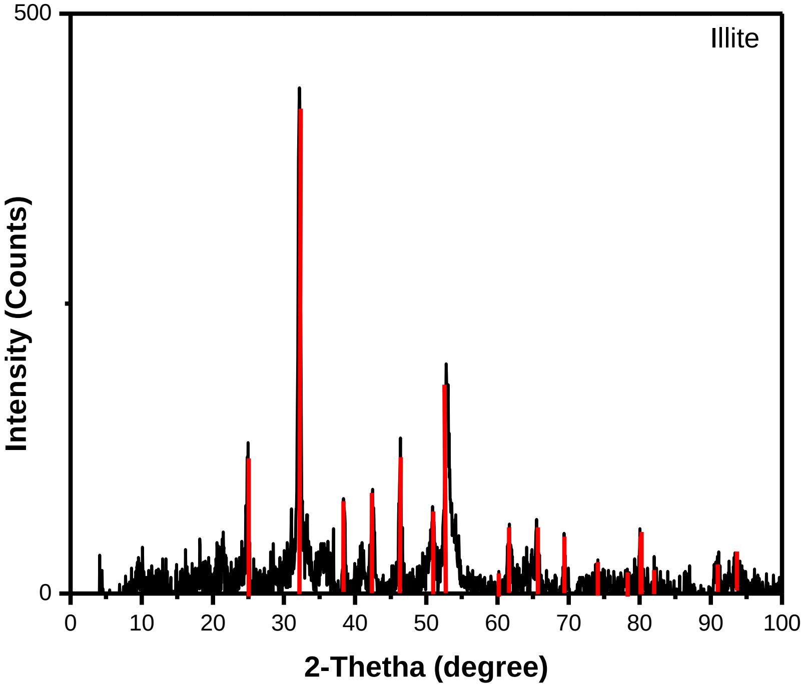
Table 4-2 The d_{50} of solids before and after grinding

Solid type	Original d_{50} µm	d_{50} after grinding µm
Kaolinite	4.58	0.13
Illite	3.78	0.16
Silica	0.25	0.25
Siderite	Chunks	0.34

4.1.2 X-ray diffraction of ground samples

XRD measurements were performed to make sure that the solid crystals have not changed during grinding process. Silica is an amorphous solid without distinct XRD pattern. The XRD patterns are shown in Figure 4-2 in which red lines represent location of peaks for the standards. The results show that the major peaks of the samples matches well with standard lines indicating that the crystal structure of clays -kaolinite and illite- and the crystal of siderite have not changed during grinding. These peaks also matched with previous study on extracted solids from bitumen froth from different ores [17]. There are some noises in the graphs because the samples were ground to very small in sizes.


Kaolinite
Intensity (Counts)
1000
500
0
0
10
20
30
40
50
60
70
80
90
100
2-Thetha (degree)


Illite
Intensity (Counts)
500
0
0
10
20
30
40
50
60
70
80
90
100
2-Thetha (degree)

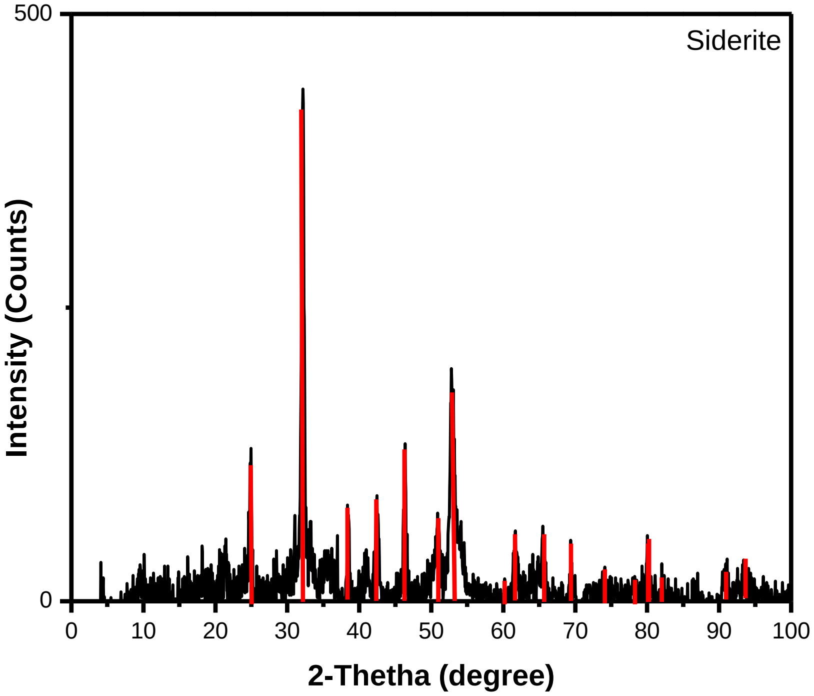


Figure 4-2 XRD pattern for kaolinite, illite and siderite

4.1.3 Treatment of samples

Prior to treatment, a solution of coker-feed bitumen and HPLC toluene at a 1:1 mass ratio was prepared and shaken over night to fully dissolve the bitumen. The bitumen in this solution contained 0.5 wt% fine solids. To obtain solid-free diluted bitumen, solution was centrifuged at 35000 g-force for two hours. Based on the Stokes equation [73] solids larger than 37 nm in diameter should be removed. The solids-free bitumen was used as stock solution and diluted using HPLC toluene to desire concentrations for the treatments of solids.

To treat the solids, each solid sample was placed in the bitumen solution, sonicated for 1 hour and shaken for 24 hours to maximize the contact between the solid particles and bitumen. Then the bitumen solution with added solids was transferred to 35 mL-centrifuge tubes. After centrifugation at 15000 g-force the solids were separated from the oil phase. After decanting the supernatant, the solids were washed by toluene to remove any oil trapped in the solids. Specifically, about 30 mL of HPLC toluene was added to the centrifuge tube. The tube was sonicated for 20 minutes and centrifuged at 15000 g-force for 15 minutes. Then the supernatant was decanted to leave the solids at the bottom of the tube. Another 30 mL of toluene was added and the washing process was repeated a couple of times until the supernatant is colorless. The number of washes depended on the initial concentration of bitumen solution in which the solid samples were treated. As a result, organics which remained on the surface of particles cannot be washed away with toluene and considered irreversibly adsorbed. After washing, the solids were kept in toluene for later use. Before any experiment, the solid sample was taken out of toluene and left to dry in a vacuum oven at room temperature for 72 hours. Figure 4-3 is a schematic summarizes this solid treatment process.

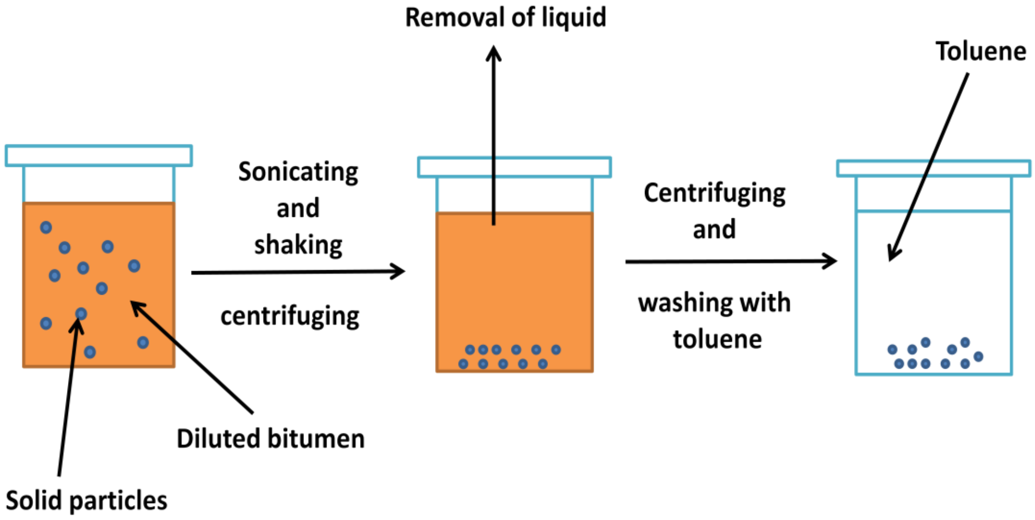


Figure 4-3 Schematics of model solids treatment process

4.2 Solid sample characterization and comparison

In this part the level of adsorption of bitumen components on the solid surface has been investigated based on four different factors:

- Solid type
- Particle size

- Water film on the particle
- Bitumen concentration

Different characterization techniques were applied to characterize the solid properties before and after the treatment.

4.2.1 Effect of solid type

Four types of solids that have been used in this study are kaolinite, illite, siderite and silica. All of these solids are naturally hydrophilic when they are not contaminated by organic compounds on their surface.

4.2.1.1 Kaolinite

The most abundant clay in oil sands is kaolinite. Its crystal building block contains one tetrahedral sheet and one octahedral sheet known as 1:1 type of clay. Since there is only limited isomorphic substitution within the layers of kaolinite, there is little permanent negative charge on the surface of this solid. Kaolinite is very hydrophilic when it is pure.

Solids-free bitumen in toluene stock solution was prepared. The concentration of bitumen was 58 wt% of bitumen, which is close to of solvent/bitumen=0.7 mass ratio as encountered in naphthenic froth treatment. Precisely weighted 5 grams of ground kaolinite was added to the 50 mL such bitumen solution to treat the solids.

After the toluene washing and drying, FTIR measurement was performed to investigate the presence of organic compounds on the clay. The results were compared with that of the pure ground kaolinite in Figure 4-4.

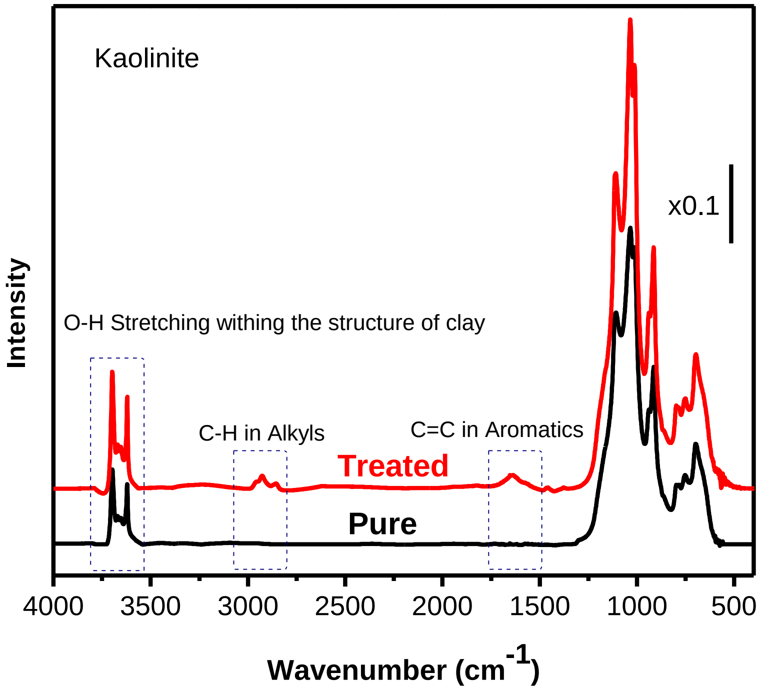


Figure 4-4 FTIR spectra of pure and treated kaolinite

The spectral differences between the pure and treated kaolinite were seen at wavenumbers of about 1600 and 2840 cm^{-1}. The peak around 1600 cm^{-1} belongs to stretching vibration of carboxylate or C=C of aromatic ring and the peak at 2840 is assigned to stretching vibration of C-H which shows the adsorption of alkyls [4].

The water contact angle of kaolinite was also changed from 0° for the pure sample to about 130° for the treated sample. This change indicates a relatively large amount of hydrocarbons that have adsorbed on kaolinite.

To evaluate the adsorption quantitatively, thermal gravity analysis (TGA) was performed. TGA determines changes in sample weight in relation to temperature by increasing temperature from 25°C to about 600°C. The amount of decrease in sample weight due to evaporation/decomposition of organics can show the organic contaminants content of on solid sample with an error less than 0.02 milligram. The problem with this method is that kaolinite structure also undergoes a change at about 400°C [74] where the O-H bond on the surface of clay dehydrogenises to form H_2O which evaporates and also cause a change in the total weight. Therefore, the total weight change is not only because of evaporation/decomposition of organics. Another method is elemental analysis using VarioMICRO elemental analyzer which can measure the weight percentage of carbon (C), nitrogen (N), hydrogen (H) and sulphur (S) in the sample. Since the amount of organic contaminants on clay surface was lower than the instrument detection limit the results could not be interpreted conclusively.

The X-ray photoelectron spectroscopy (XPS) measures the chemical composition of the clay surface in the terms of atomic concentration with detection depth of 20 nm. The detection limits for most of the elements are in the parts per thousand-range. Therefore this technique was chosen to determine the contamination for all the samples. Table 4-3 shows the elemental analysis results by XPS for pure and treated kaolinite.

Table 4-3 Elemental analysis on pure and treated kaolinite by XPS

Elements	**Pure kaolinite Mass concentration %**	**Treated kaolinite Mass concentration %**
Na	0.61	0.06
O	50.8	37.16
C	8.5	45.05
Si	22.88	8.48
Al	17.21	9.25

Comparison between two sample shows that the mass concentration of carbon increased from 8.5 wt% to about 45 wt%. At the same time, concentration of Si and Al decreased. Detection of Si and Al means that either there are free areas on the clay surface that are not covered by bitumen components or the layer of contamination is thinner than 20 nm.

4.2.1.2 Illite

The second common clay in oil sands is illite. In crystal of illite there is an octahedral sheet between 2 layers of tetrahedral sheets so it is 2:1 type of clay. Unlike kaolinite, ¼ of Si in tetrahedral sheets are substituted by Al so there are permanent negative charges on the clay surface.

The treatment process is similar to kaolinite treatment as 5 grams of ground illite was added to 50 mL of solids-free bitumen solution with 58 wt% bitumen and shaked. After the six toluene wash-cycle and 72 hours of drying in a vacuum oven FTIR experiment was performed.

In Figure 4-5 the comparison of two FTIR spectra of pure and treated illite is shown. Just like that of kaolinite, two peaks around 1600 cm^{-1} and 2800 cm^{-1} appeared in the treated illite that represent stretching vibration of C=C in aromatics and C-H in alkyls respectively on the basis of FTIR spectra of Athabasca bitumen and its components reported in Literature [4]. This means these two clays tend to adsorb same type of bitumen components on their surface under same condition.

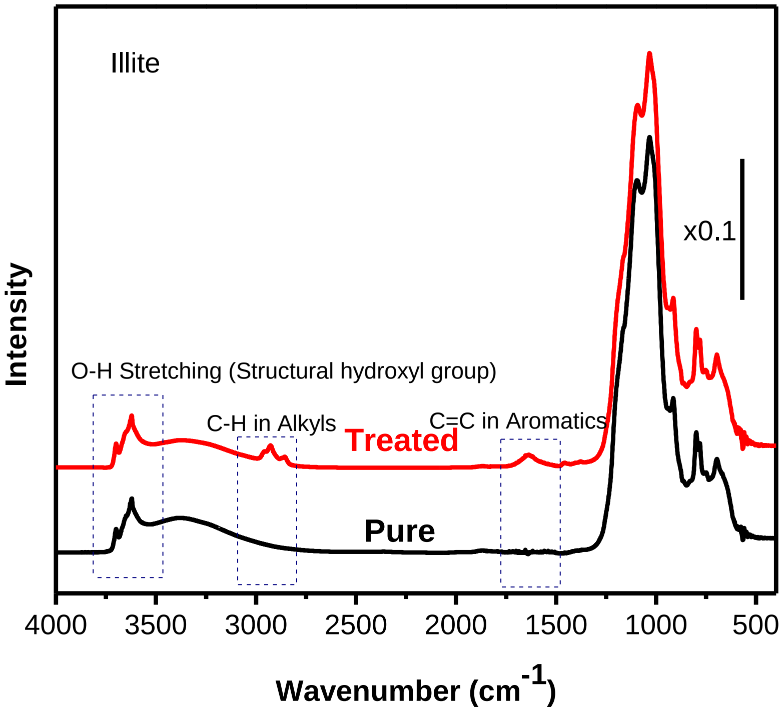


Figure 4-5 FTIR spectra of pure and treated illite

To determine the change in wettability of the solid sample before and after the treatment, water contact angle was measured. Illite is very hydrophilic in its pure phase and water droplet spreads very fast on the illite coated wafer so the water contact angle is almost 0°. But after the treatment the sample became hydrophobic and the contact angle measured was 111°.

The elemental analysis of pure and treated illite is summarized in Table 4-4. The carbon concentration on the surface increased after the treatment and Si and Al concentration decreased as it was expected. Potassium was detected because the layers of illite are bonded by K^+; its concentration remained constant, which means that the bonds were stable during the treatment.

Table 4-4 Elemental analysis on pure and treated illite by XPS

Elements	Pure illite Mass concentration %	Treated illite Mass concentration %
Na	0.31	0.23
Fe	3.62	3.24
F	2.88	2.86
O	47.67	34.14
Ca	0.75	0.77
K	3.96	3.59
C	5.35	33.81
S	0.43	1.54
Si	22.89	13.14
Al	12.14	6.67

4.2.1.3 Siderite

The amount of siderite in oil sands may not be significant but this mineral is problematic especially in froth treatment process as it is more found in organic phase than in tailings [27]. It can also form very stable water in oil emulsions so it is interesting to study adsorption of bitumen components on the surface of siderite.

Siderite treatment process took 24 hours shaking and 2 hours sonicating, similar to that of kaolinite and illite. After the sample was dried FTIR test was performed on both treated and pure siderite. As seen in Figure 4-6 there are two major peaks on the treated solid diagram which did not appear on the pure sample graph.

These two peaks are similar to the previous cases, one at 1600 and one at 2840 cm^{-1} which represent stretching vibration of C=C of carboxylate compounds or aromatic ring and C-H of alkyls respectively.

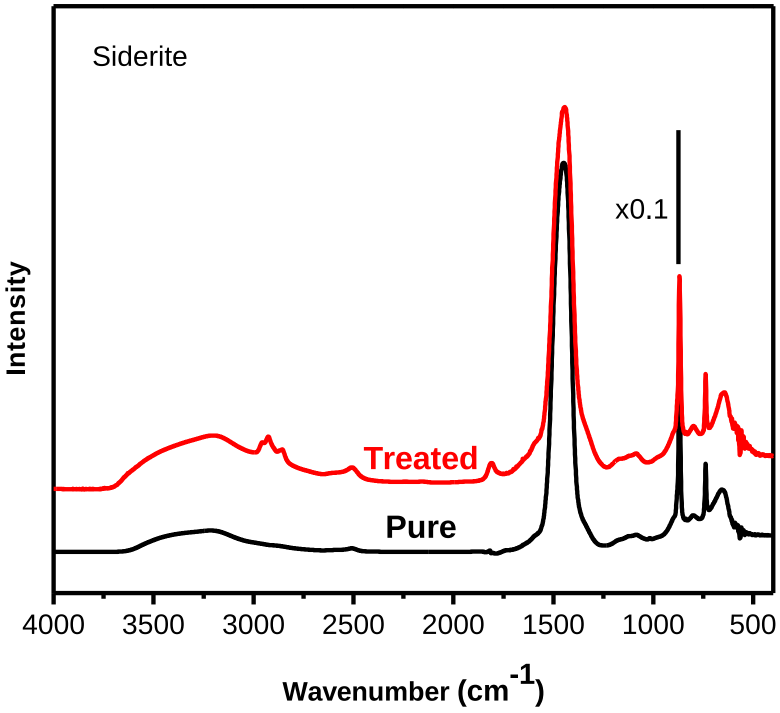


Figure 4-6 FTIR spectra of pure and treated siderite

Pure and treated siderite has also shown big difference in terms of wettability. Pure sample of siderite is hydrophilic and has a water contact angle of 0°. However after exposure to the bitumen solution with 58 wt% bitumen, its water contact angle increased to 115°.

Table 4-5 Elemental analysis on pure and treated siderite by XPS

Elements	**Pure siderite** **Mass concentration %**	**Treated siderite** **Mass concentration %**
Na	0.03	0.22
Fe	45.29	30.48
Mn	3.94	3.64
O	33.68	27.66
Ca	0.92	1.24
C	13.30	31.77
S	0.78	2.13
Si	1.69	1.50
Al	0.37	1.36

Elemental analysis by XPS, as shown in Table 4-5, is complicated in the case of siderite since it has carbon in its structure. Organic compounds covering the mineral surface would lead to an increase in the carbon concentration. However the lower concentration of Fe shows the coverage of siderite surface by bitumen components.

4.2.1.4 Silica

Since in most of studies Silica was used as the model solid in oil water emulsions, it was chosen as one of the four solid samples in these experiments. The silica used in these series of experiments is amorphous and it does not have crystal structure.

Silica sample was treated by 58 wt% bitumen in toluene solution. Similar to the procedure that was used for kaolinite, illite and siderite, it was washed with toluene for six cycles and dried in vacuum oven for 72 hours. FTIR diagram of treated and pure silica is illustrated in Figure 4-7.

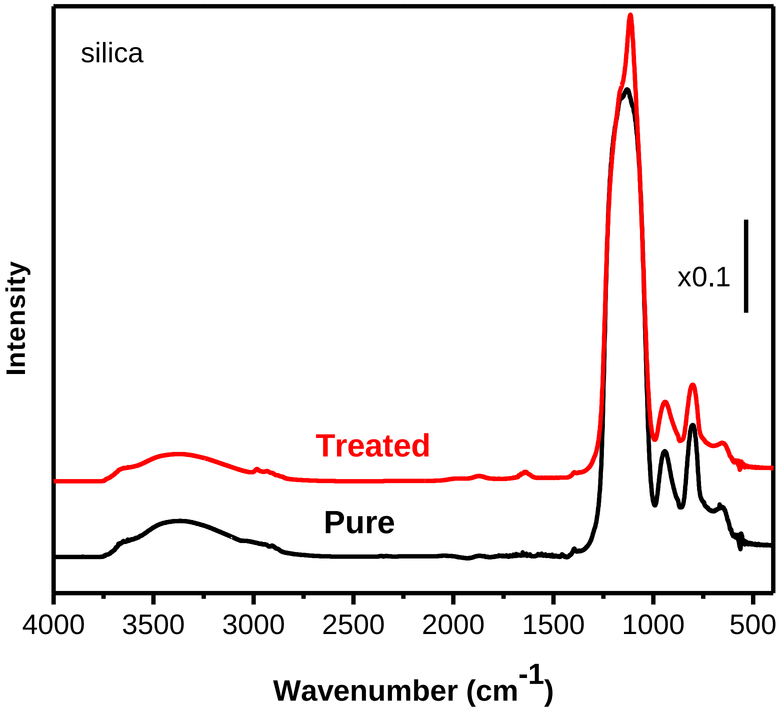


Figure 4-7 FTIR spectra of pure and treated silica

Unlike other solid samples, there is not a distinctive difference between the two FTIR spectra for treated and pure sample of silica. The peak at 2840 cm^{-1} is not very strong so it can be concluded that there is not much adsorption of alkyls on the surface of silica. However stretching vibration of C=C is still present on treated silica IR spectra.

The water contact angle measured for treated silica is 102° compared to 0° for the pure sample.

Table 4-6 Elemental analysis on pure and treated silica by XPS

Elements	Pure silica Mass concentration %	Treated silica Mass concentration %
O	54.11	46.30
C	5.03	16.09
S	0	1.71
Si	40.86	35.89

Elemental analysis in Table 4-6 demonstrates the increase in carbon concentration on the surface of treated silica due to adsorption of organic compounds. Also the presence of sulphur is clearer in the silica case compared to the other solids.

It can be concluded that kaolinite, illite, siderite and silica all adsorb organic components from bitumen on their surface. However there is a slight difference for silica where there is no IR peak at 2840 cm^{-1}. Table 4-7 summarizes the final water contact angles for four samples.

Table 4-7 Water contact angles of model solids after the treatment

Samples	Contact angle (degree)
Ground kaolinite	130
Ground illite	111
Ground siderite	115
Silica	102

Considering all solid samples had the water contact angle of 0° before their treatment form, kaolinite had the highest change in wettability. One hypothesis is that there is almost no charge on tetrahedral sheet in kaolinite. As a result, its tendency to adsorb hydrocarbons from bitumen is higher [75]. Illite and siderite are close in term of water contact angle, and silica is the least hydrophobic sample compared to the other three samples.

As it was mentioned before, kaolinite is the most abundant mineral in Athabasca oil sands and also showed the highest level of adsorption of bitumen components on its surface. Therefore rest of the study is focused more on kaolinite.

4.2.2 Effect of solid size

The original and ground kaolinite were treated as described in section 4.1.3 using 58 wt% bitumen in toluene solution. The kaolinite particles of two samples were washed with HPLC toluene for six times. The only difference between these two samples was their size. The d_{50} was 4.58 µm for the original kaolinite and 129 nm for the ground kaolinite. Both solids are very hydrophilic and their water contact angle is 0° when they are not treated.

Fourier transform spectroscopy was performed on both samples to investigate the organic adsorption on their surfaces. Figure 4-8 shows that there is no difference between FTIR spectra of the solids samples. They both have peaks at 1600 and 2840 cm^{-1} which represent presence of C=C in carboxylates or aromatics and C-H in alkyls, respectively. This finding is anticipated as both were expected to be contaminated similarly.

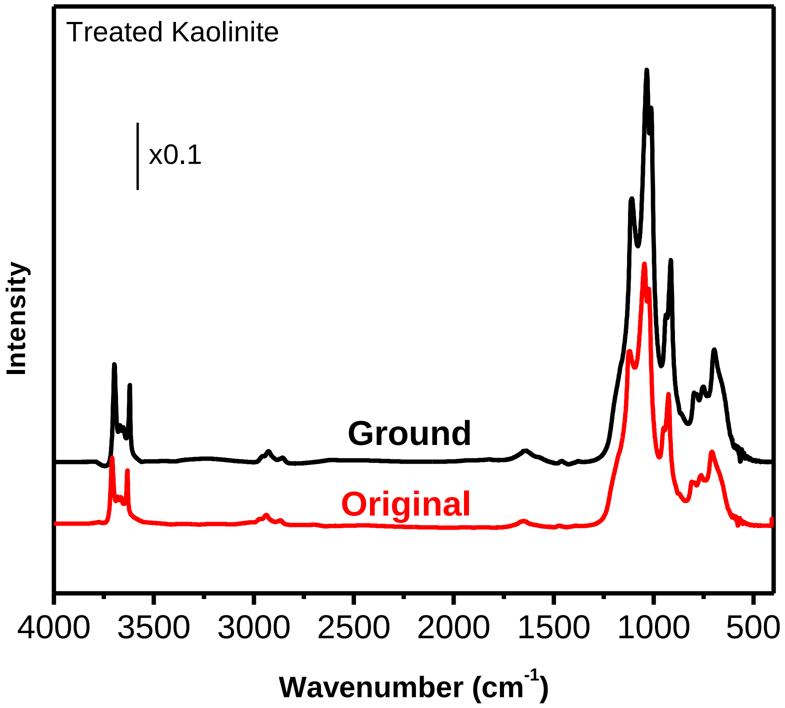


Figure 4-8 FTIR spectra of original and ground treated kaolinite

Since the adsorption of bitumen components on both samples is similar it can be expected that the change in wettability is also similar. Table 4-8 shows treated original and ground kaolinite with only 3° difference water contact angle between coarse and fine kaolinite contaminated with bitumen in toluene solutions.

Table 4-8 Final contact angles for two sizes of treated kaolinite

Samples	**Size (d_{50}) (micron)**	**Contact angle (degree)**
Original kaolinite	4.58	127
Ground kaolinite	0.130	130

Although the original kaolinite is 35 times larger than ground kaolinite, the results from elemental analysis in Table 4-9 show that carbon concentration is almost similar in both cases. The similar results obtained from contact angle and XPS measurement suggested that the particles size in this range has negligible effect on contamination of kaolinite by bitumen in toluene solution and this is in agreement with previous work findings [14].

Table 4-9 XPS results for treated kaolinite in two sizes

Elements	Treated original kaolinite Mass concentration %	Treated ground kaolinite Mass concentration %
Na	0.12	0.06
O	35.90	37.16
C	44.19	45.05
Si	8.85	8.48
Al	10.94	9.25

4.2.3 Effect of water around the particle

Since solid particles in the oil sands ores are separated from the bitumen by a thin layer of water [2; 29], the wetting condition of solid is one of the factors considered when studying the adsorption of bitumen components on a solid surface. In this section the effect of a water film around the kaolinite particles on particle contamination by bitumen is investigated.

In this set of tests, solid sample with adsorbed water film on its surface was prepared by placing 5 grams of ground kaolinite powders in a filter cone. The cone with the sample was placed on top of a beaker containing boiling water. As the water evaporated and passed through the solid layer, the water vapor condensed on clay particles to form a layer of water film due to the extremely hydrophilic nature of the kaolinite surface. The schematic view of experimental set up is shown in Figure 4-9. Right after sample preparation, the ground kaolinite with water film was placed into the 58 wt% bitumen in toluene solution where it is treated in the same way as treating dry kaolinite.

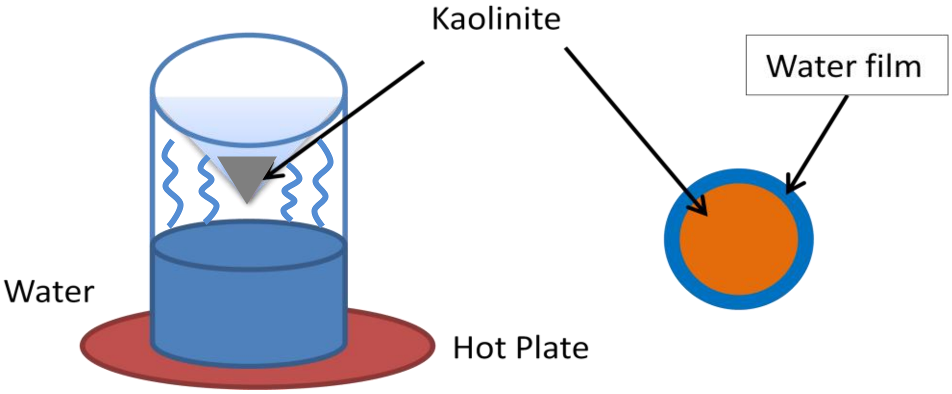


Figure 4-9 Schematic view of wet kaolinite preparation

Compared with dry kaolinite, the FTIR spectra of the wet kaolinite sample in Figure 4-10 shows a negligible contamination of the wetted kaolinite by hydrocarbons of bitumen. There is not much contamination of the wetted sample except for the weak peak at 1600 cm^{-1}. This finding suggests that the water film on clay particles prevented adsorption of bitumen components on the kaolinite surface.

Wettability measurements of contaminated kaolinite samples also confirmed that the water film around the clay particle acted as a shield and kept the clay hydrophilic, as shown by the water contact angle which remained 0° even after the treatment. This is in great contrast to dry clay treated under the same condition with a water contact angle of 130° due to contamination of dry kaolinite by bitumen components.

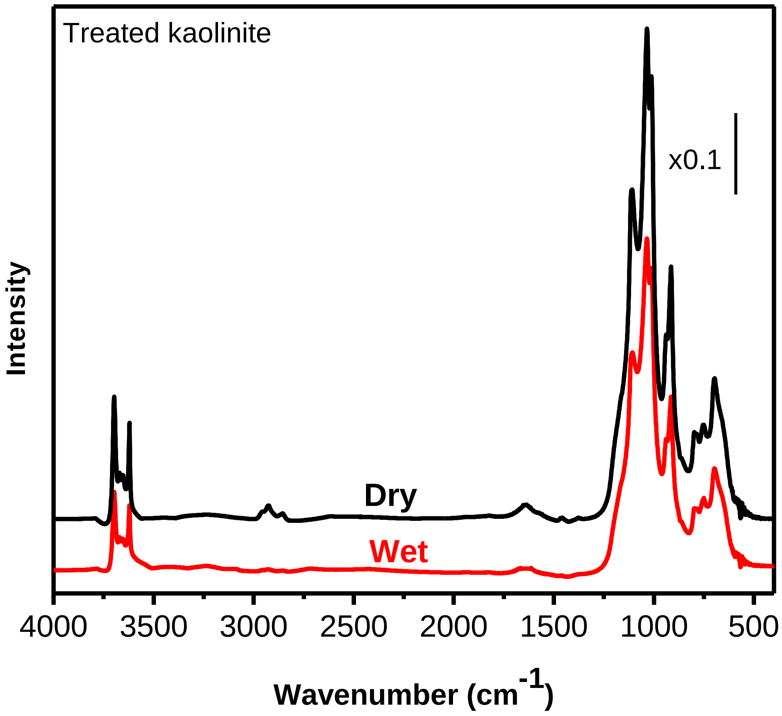


Figure 4-10 FTIR spectra of dry and wet treated kaolinite

Elemental analysis did not detect much carbon on the wetted kaolinite surface. On the other hand, dry treated sample contained 48 wt% carbon on its surface.

Table 4-10 XPS results for wetted and dry treated kaolinite

Elements	**Wet treated kaolinite** **Mass concentration %**	**Treated kaolinite** **Mass concentration %**
Na	0.61	0.06
O	50.8	37.16
C	10.5	45.05
Si	21.88	8.48
Al	16.21	9.25

4.2.4 Effect of bitumen concentration

In addition to solid surface properties, bitumen content in diluted bitumen solution may change the level of contamination. To examine the effect of bitumen concentration on kaolinite contamination, five solid free-bitumen in HPLC toluene solutions with different bitumen contents were prepared. Then 5 grams of ground kaolinite were added to each solution. All samples were shaken and sonicated using procedures described in the previous in the treatment process and washed with toluene. The number of washing cycles was different for each sample since they had different bitumen contents.

Table 4-11 shows the initial bitumen concentration for each sample and its final water contact angle. Each treated sample was named after its water contact angle for future references.

Table 4-11 Samples water contact angle for different bitumen concentrations

Mineral used	Treated by diluted bitumen (wt %)	Contact angle (degree)	Samples
Ground kaolinite	0	0	T-K-0
	1	23	T-K-23
	8	68	T-K-68
	20	105	T-K-105
	58	130	T-K-130

Where there was no bitumen in solution the treated kaolinite remained hydrophilic with contact angle of 0°. FTIR spectra of this sample in Figure 4-11 also confirmed that there was not a considerable adsorption of organics on the surface of the clay.

By adding 1 wt% bitumen to the system, kaolinite started to adsorb bitumen components and that was the reason for the increase in water contact angle to 23°. Further addition of bitumen caused higher adsorption of more organic compounds, which resulted in stronger peaks at 1600 and 2840 cm^{-1} in FTIR spectrum for each sample, indicating increasing content of C=C of carboxylate or aromatics and C-H of alkyls. Water contact angle measurements also illustrated that the higher bitumen content present initially in the treatment process, led to more hydrophobic clay surfaces.

It also should be noted that in concentrations higher than 58 wt% bitumen no increase in contamination on surface occurred. It can be explained by: the adsorption capacity of organics reaching its limit. Therefore no higher contact angle than 130 ° was observed in these experiments.

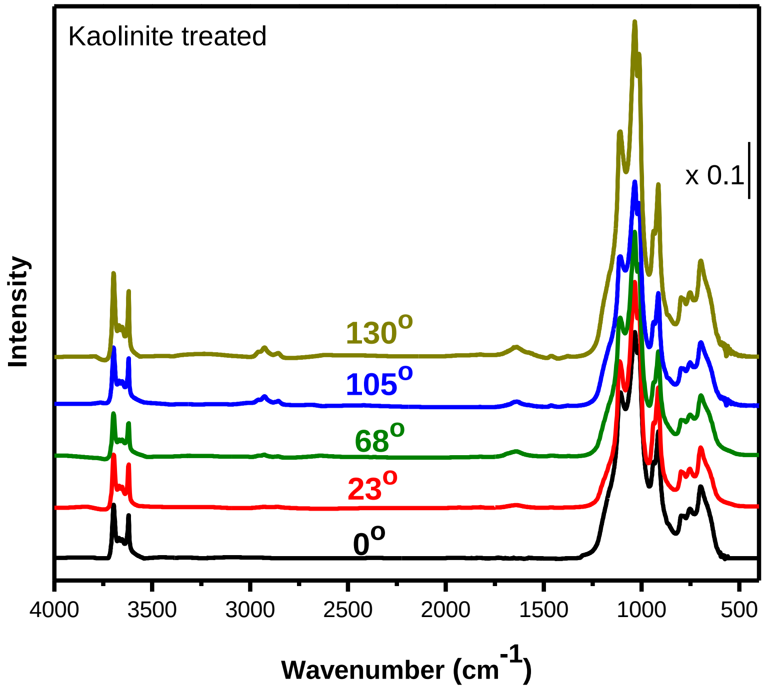


Figure 4-11 FTIR spectra of treated kaolinite samples with different hydrophobicities

Elemental analysis also confirmed that higher bitumen concentration lead to greater adsorption of more organic compounds as shown by increasing the carbon concentration from 8.5 wt% on the hydrophilic solid to about 45 wt% on the most hydrophobic solid sample. Simultaneously, Si and Al concentrations decreased due to increased coverage of the solid surface by bitumen components. This result is in agreement with Tu's work that higher concentration of pentane insoluble organic matters led to more carbon detection on kaolinite and illite surfaces [34].

Table 4-12 XPS results for treated kaolinite with different hydrophobicities

Elements	**T-K-0** **Mass concentration %**	**T-K-23** **Mass concentration %**	**T-K-68** **Mass concentration %**	**T-K-105** **Mass concentration %**	**T-K-130** **Mass concentration %**
Na	0.61	0.37	0.19	0.12	0.06
O	50.8	44.04	41.52	39.10	37.16
C	8.5	21.96	28.83	33.05	45.05
Si	22.88	17.33	14.58	13.48	8.48
Al	17.21	16.30	14.88	14.25	9.25

4.3 Summary

In this chapter the tendency of four types of solids to adsorb bitumen components on their surface was studied. Major factors affecting the adsorption were studied and discussed, including:

- Effect of solid type:

All samples, kaolinite, illite, siderite and silica became contaminated during the treatment by diluted bitumen. However kaolinite had the greatest increase in water contact angle compared to the other three types of solids.

- Effect of solid size:

Original and ground kaolinite showed similar level of contamination and close water contact angle values. It can therefore be concluded that the size of solid particles does not impact the adsorption of organics on the surface.

- Effect of water film around solid particles

In the case of wetted kaolinite, the water film around the clay particles acted as a shield and prevented the contamination, therefore this sample remained hydrophilic after treatment. On the other hand, dry kaolinite adsorbed bitumen components and became hydrophobic.

- Effect of bitumen concentration

Increasing in bitumen content of initial diluted bitumen solutions leads to a higher level of organics adsorption on the kaolinite. Therefore by changing the bitumen concentration it was possible to obtain kaolinite samples with different water contact angles ranging from 0° to 130°.

In the next chapter the role of aforementioned solids in the formation of model emulsion will be discussed. This would help to understand the role of solids with different level of contamination in emulsion stabilization.

5 Emulsion formation

In the previous chapter adsorption of bitumen components on the surface of model solids was investigated. As discussed in section 4.2, all four types of solids adsorbed organics on their surface when dry. In the case of kaolinite, the size of the clay does not affect the adsorption. However water film and bitumen concentration were the important factors.

In this chapter, the previously prepared solid samples of different types and hydrophobicities were used to form emulsions in water-oil system. The study considered emulsion stability as a function of solids, bitumen concentration in oil phase, pH of aqueous phase and the ratio of aqueous phase to oil phase. These investigations revealed the importance of different factors in the formation of stable emulsions.

To prepare an emulsion, the oil phase and water phase at a specified volume ratio were added to a 20 mL vial and mixed at 13000 rpm using a homogenizer for 5 minutes. Certain amount of solids was added to the mixture at the time the homogenizing started. The emulsion was transferred to a graduated cylinder and left until it reached equilibrium where there was no significant change in the volume of partitioned phases.

5.1 Effect of bitumen content

The effect of bitumen concentration in the oil phase on the emulsion formation was studied. To perform the test 8.4 mL diluted bitumen and 3.6 mL DI water were added to a vial. While oil and water were mixed at 13000 rpm, 0.012 g of ground kaolinite treated with diluted bitumen with contact angle 105° was added to the system and the mixing continued for 5 minutes. Each sample contained:

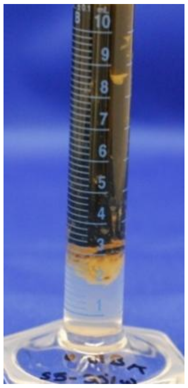
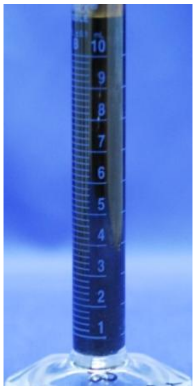
- 70 vol% oil phase
- 30 vol% aqueous phase

- 1 g/L solid T-K-105

Bitumen content in each sample was the main variable. The photo of each emulsion sample and the associated bitumen concentration is shown in Table 5-1. The photos were taken after about 20 hours when there was no change in the volume of released water and emulsion phase. The emulsion volume as a distinct middle layer between oil and water phase was recorded.

If the droplets in the emulsion are not very stable, the emulsion volume would be low since the droplets would readily coalesce with each other and the bulk water phase. On the other hand, if the droplets are stable, they would not coalesce and as a result high volume of emulsion would be observed. Therefore emulsion volume could be used as an indicator of emulsion stability [53].

Table 5-1 Emulsion sample prepared with different bitumen content in the oil phase with 1g/L kaolinite of contact angle 105°

				
0 wt% Bitumen	0.1 wt% Bitumen	10 wt% Bitumen	33 wt% Bitumen	58 wt% Bitumen

As shown in Table 5-1, there was little emulsion formed in the absence of bitumen. In fact the solids partitioned at planar oil-water interface. This finding suggests that hydrophobic kaolinite does not stabilize emulsions in the absence of surfactants. By adding bitumen to the oil phase, emulsions began to form. Increasing bitumen content in the oil phase led to an increase in emulsion volume as shown in Table 5-1 and Figure 5-1.

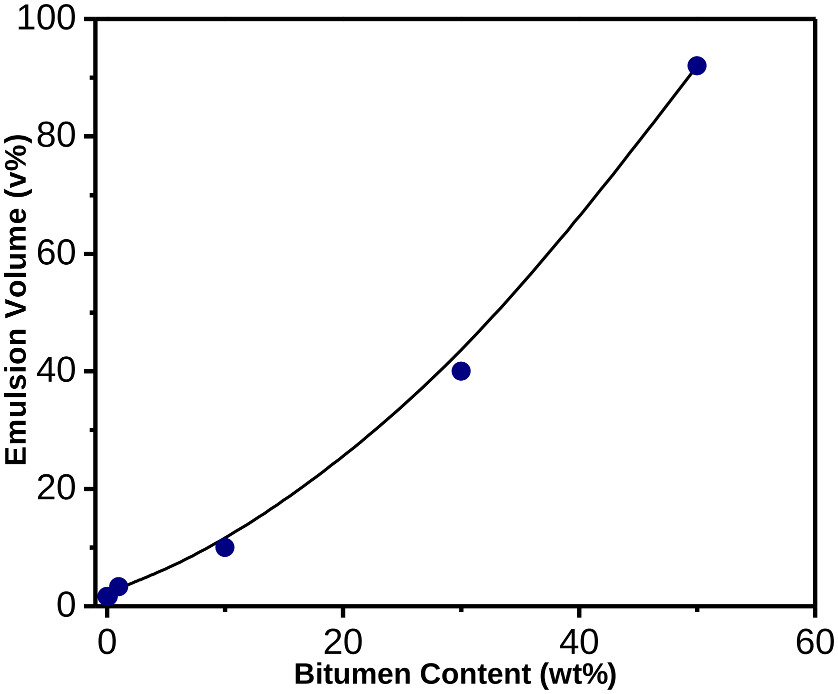


Figure 5-1 Effect of bitumen content on emulsion volume

Figure 5-1 also showed that the emulsion volume for the first three samples was much less compared with the other two samples. These can be explained by the assumption that:

- Adding bitumen to the system leads to increase surface active compounds at the oil-water interface.

By increasing bitumen content, the concentration of natural surfactants in bitumen and surface active components increased, which results in better stabilized water droplets in the oil phase and higher volume of emulsions.

- Another effect of bitumen addition and as a result increasing surfactants concentration in the system was reduction in interaction energy between particles. As a result, the particles were better dispersed.

To form a stable emulsion, solids should assemble at surface of water droplets to prevent coalescence. Therefore, solids must disperse well and cover water droplets. However the formation of a network between solids prevents proper dispersion of the particles. Lucassen-Reyners et al. in their paper [63] explained that solids networks form almost immediately after emulsification has ceased. The absence of any repulsion force between solids led to network formation at a much faster rate than water droplet formation. He showed that by adding surfactants, van der Waals attraction energy of solid particles decreased since the average particle distance in the presence of surfactant increased. Therefore it took longer for the particles to flocculate.

In our system, the same phenomena could be operating. Adding bitumen would result in a better dispersion of solids. As a result, there would be a higher surface coverage on the water droplets, leading to more stable droplets and hence higher volume of emulsions.

Since bitumen content showed distinct effect on emulsion formation with kaolinite T-K-105 addition, two bitumen concentrations, 0.1 wt% (low bitumen content) and 33 wt% (high bitumen content) were chosen to test if solid wettability would affect the emulsion.

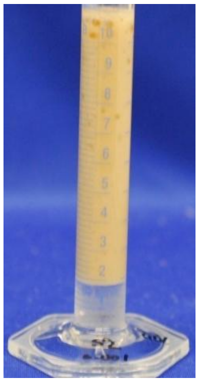
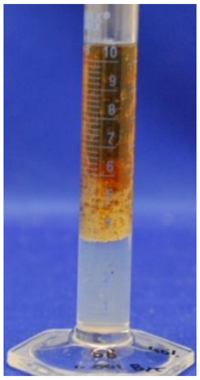
5.1.1 Effect of solids wettability on emulsion volume at low bitumen content

Since the emulsion does not form with hydrophobic kaolinite without bitumen, it is better to start with 0.1 wt% bitumen in toluene as the oil phase. In this set of tests, 8.4 mL of oil phase and 3.6 mL of DI water were mixed in a 20 mL vial. As shown in Figure 5-2, without addition of solids there was no stable emulsion formed. That means that at low bitumen content where the surfactant concentration was very low, solids were essential to stabilize the emulsion.

Figure 5-2 No emulsion in the absence of solids

With the addition of kaolinite solids treated with the same diluted bitumen stable emulsions formed to varying degrees for each solid as shown in Table 5-2. It should be noted that each solid sample was named after its contact angle. For example T-K-68 refers to kaolinite with the contact angle of 68° after treated with diluted bitumen.

Table 5-2 Emulsions prepared at low bitumen content with kaolinite of different contact angles

				
T-K-0	T-K-23	T-K-68	T-K-105	T-K-130

Addition of kaolinite led to formation of emulsion. To determine the type of emulsions, one drop of emulsion phase was added to either water or toluene. The phase in which the droplet dissolved was known as the continuous phase. Figure 5-3 illustrates a drop of emulsion formed using T-K-0 in water and toluene. In this case the drop completely dissolved in water. However it remained a clear drop in the toluene. This finding means that the emulsion is water continuous. All the emulsions were found to be oil-in-water.

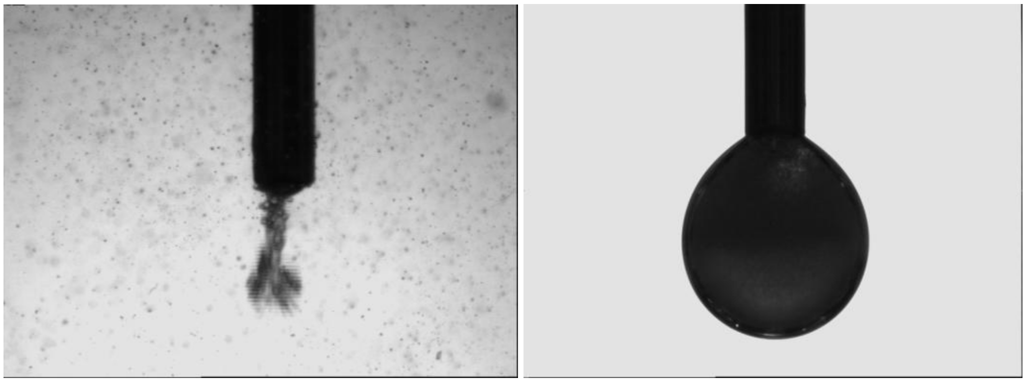


Figure 5-3 a) A drop of the sample emulsion in water b) A drop of the sample emulsion in toluene

As shown in Figure 5-4, hydrophilic solids T-K-0, T-K-23 and T-K-68 formed high volume emulsions, which mean they were capable of stabilizing oil-in-water. Between these three samples, the solid with highest contact angle, T-K-68 led to formation of highest volume of emulsion. Since this sample was hydrophilic ($\theta<90°$) but still had organic compounds on the surface of particles, it is easier for them to stay at oil-water interface. In fact the wettability of solids would affect stability of dispersed droplets. This finding is consistent with theoretical predictions: hydrophilic particles stabilize oil-in-water emulsions, and contact angle closer to 90° forms the most stable emulsions.

Hydrophobic samples, on the other hand, did not form emulsions of high volume. T-K-105 and T-K-130 could not stabilize oil drops in water. The volume of emulsions resulted from these two solids are less than 15% it is known that hydrophobic solids prefer oil continuous emulsions and are capable of stabilizing o/w emulsions.

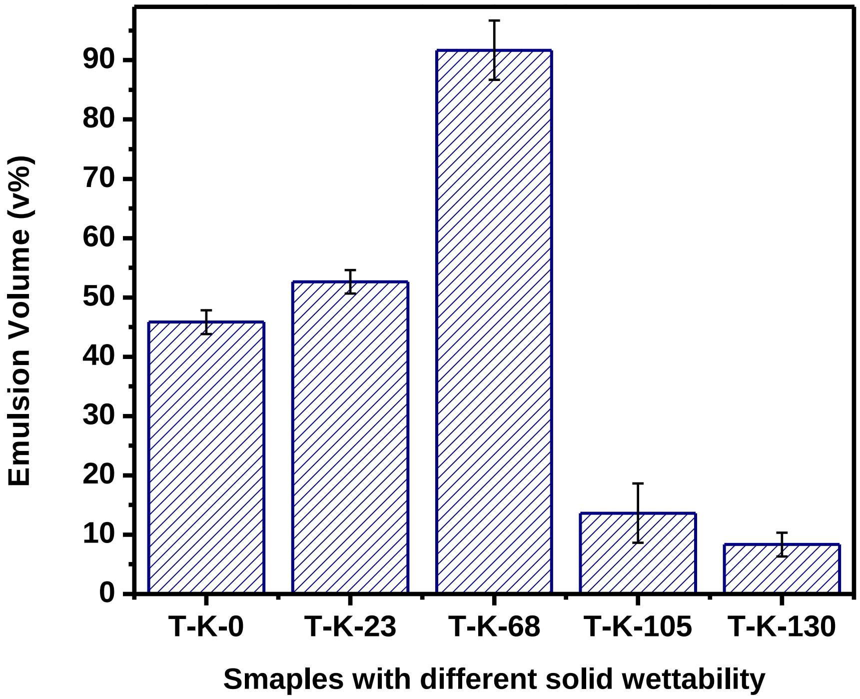


Figure 5-4 Comparison of emulsion volume for samples with different hydrophobicities

It can be concluded that with low bitumen content in oil phase and presence of solids oil in water emulsion forms. However, only hydrophilic solids can stabilize this type of emulsion.

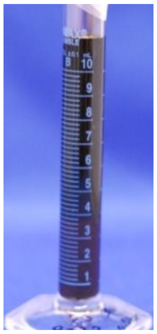
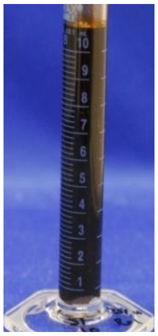
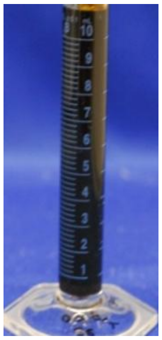
5.1.2 High bitumen content

To study the effect of solids in a system that is more similar to industrial operations, the emulsion was prepared using oil phase containing 33 wt% bitumen oil phase. For each sample, 8.4 mL oil, containing 33 wt% diluted bitumen in toluene was mixed with 3.6 mL DI water at 13000 rpm. While mixing, 0.012 g dry powder solid was added to the mixture. The mixing continued for 5 minutes, after which, the mixture was transferred to a graduated cylinder and left until the system reached its equilibrium. The results are shown in Table 5-3.

With high bitumen content very stable emulsions formed in all samples. The type of emulsion formed was water in oil as demonstrated by method shown in Figure

5-3. At high bitumen concentration, the amount of natural surfactants released is sufficient to form stable water in oil emulsion. However, the presence of solids can strengthen the interfacial film as will be shown by emulsion stability test in section 5.2.

Table 5-3 Emulsions prepared at high bitumen content with kaolinite of different contact angles

					
No solid	T-K-0	T-K-23	T-K-68	T-K-105	T-K-130

Since this study was focused more on stability of water droplets in the froth treatment process, a high bitumen content was chosen as the oil phase to study the effect of solids in the water-in-oil emulsions. On a short time basis, the emulsion volumes for all the samples were very similar. Thus instead of emulsion volume micropipette technique was used to evaluate the emulsion stability.

5.2 Solid wettability

As shown in Table 5-3, the five emulsions were prepared as described in 5.1.2 with kaolinite particles of different hydrophobicities and oil containing 33 wt% bitumen in toluene. All of the emulsions were water in oil emulsions.

Since emulsion volume was not conclusive with regards to stability, the micropipette technique was used instead to determine droplet stability by manipulating individual water droplets inside the emulsion. In this method, two water droplets were held by two micropipettes and pressed to contact with each other for 20 seconds and then pulled away. During contact of the water droplets, coalescence might or might not occur, depending on the stability of the emulsion. To quantify the stability of water droplets in each sample, the probability of coalescence is determined as:

$$\textit{Probability of coalescence} = \frac{\textit{Number of droplets that coalesced}}{\textit{Total number of tests (30)}}$$

To perform the micropipette test 50 µL of each emulsion was diluted by 10 mL HPLC grade toluene then transferred to a glass slide and placed under the microscope to determine probability of coalescence for at least 30 pairs of water droplets.

Figure 5-5 shows the probability of coalescence for each emulsion sample. The first bar corresponds to the sample that had no solids. This sample was used as a control to better understand the role of solids. The probability of coalescence of droplets in emulsion formed by T-K-0 was higher than control sample, which means that the addition of these solids enhances the rate of coalescence and hence would reduce emulsion stability. From this observation it can be concluded that very hydrophilic kaolinite with no contamination does not tend to stabilize water-in-oil emulsion. Instead, these very hydrophilic solids preferred to stay inside water droplets, which explains the higher probability of coalescence. It should be noted that, addition of dry solids to a system which contained diluted bitumen might cause extra contamination, but there was still difference between solids with different contact angles.

With increasing contact angle the probability of coalescence was observed to decrease. It is interesting to note that treated kaolinite with contact angle 105° resulted in the most stable droplet. This makes sense since the solids are hydrophobic and hence more favorable to stabilize water droplets in oil.

T-K-105 and T-K-130 were both hydrophobic but T-K-130 had a higher probability of coalescence. It can be explained by equation (1) which confirms that the energy of adsorption of a particle at an oil-water interface is higher when the contact angle of the particle is closer to 90°.

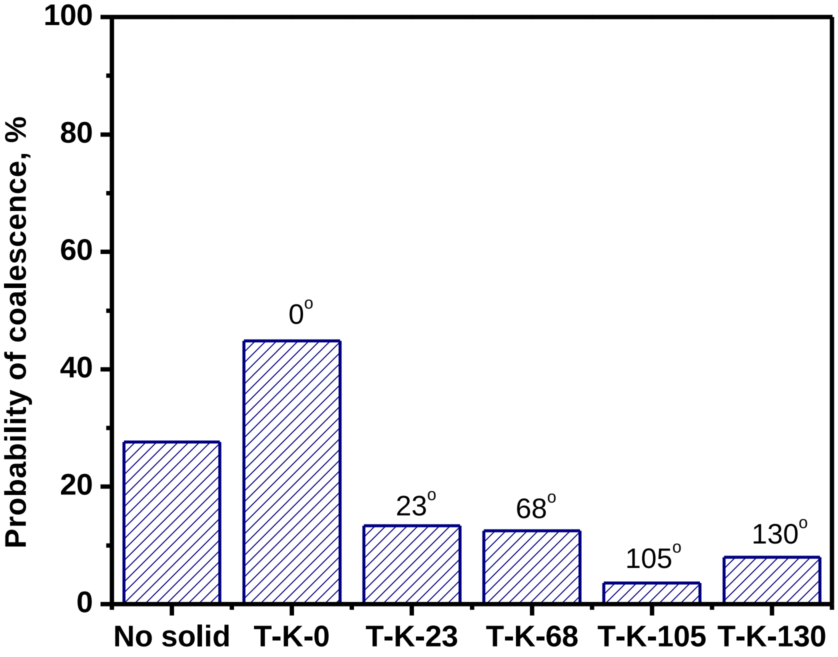


Figure 5-5 Probability of coalescence for emulsions with solids of different hydrophobicities

5.3 Solid type

As stated in chapter 4, model solids that were used in this study are kaolinite, illite, siderite and silica. It was shown that, although four types of solids are different in surface properties and shape, all of them adsorbed bitumen components on their surface and became hydrophobic. In this section, the contaminated samples were used to form emulsions and the emulsion stability was compared.

For each solid sample, 8.4 mL of oil phase and 3.6 mL of DI water were added to a 20 mL vial. While mixing two phases, 0.012 g of dry solids was added to the system. So each mixture held 1 g/L solid, 30 vol% aqueous phase and 70 vol% oil phase which contained 33 wt% bitumen. The blends were transferred to graduated cylinders and left 20 hours to reach equilibrium.

Figure 5-6 compares the probability of coalescence of all four samples. The number on top of each bar represents the contact angle value for each solid.

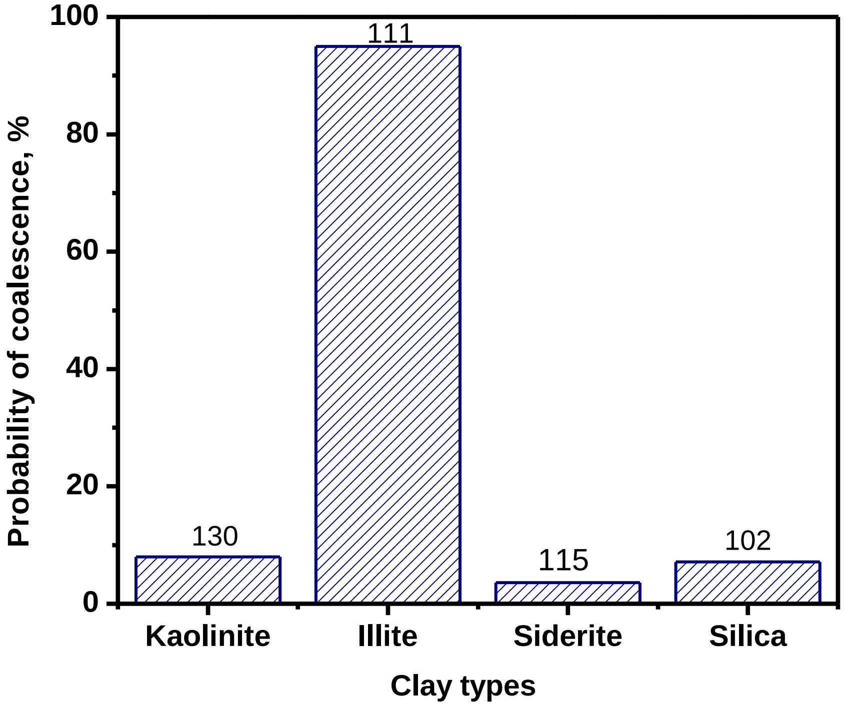
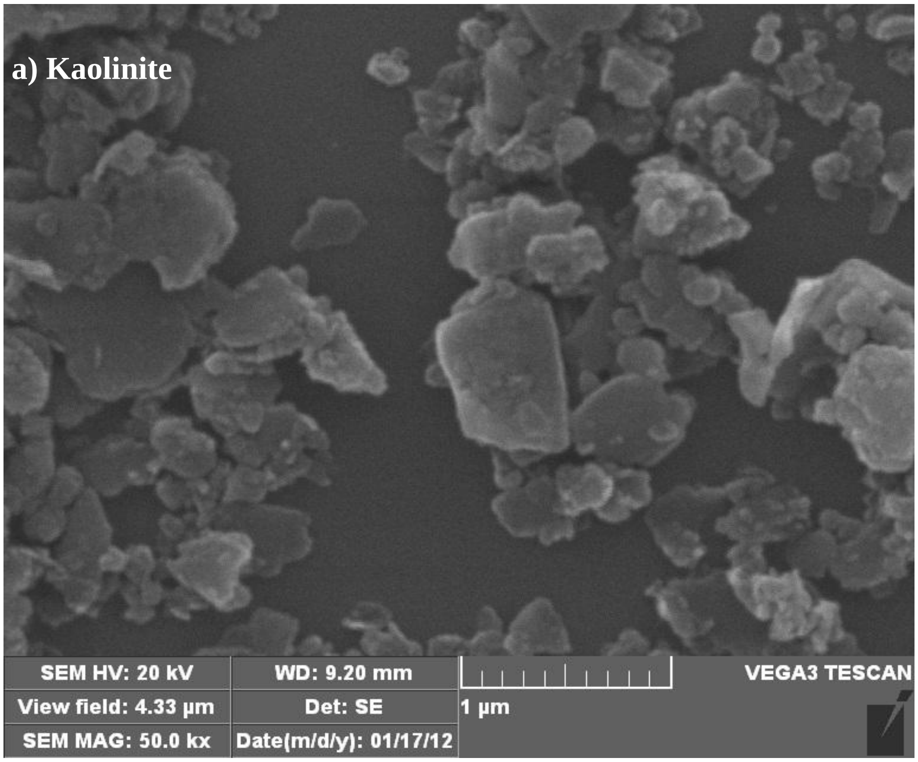
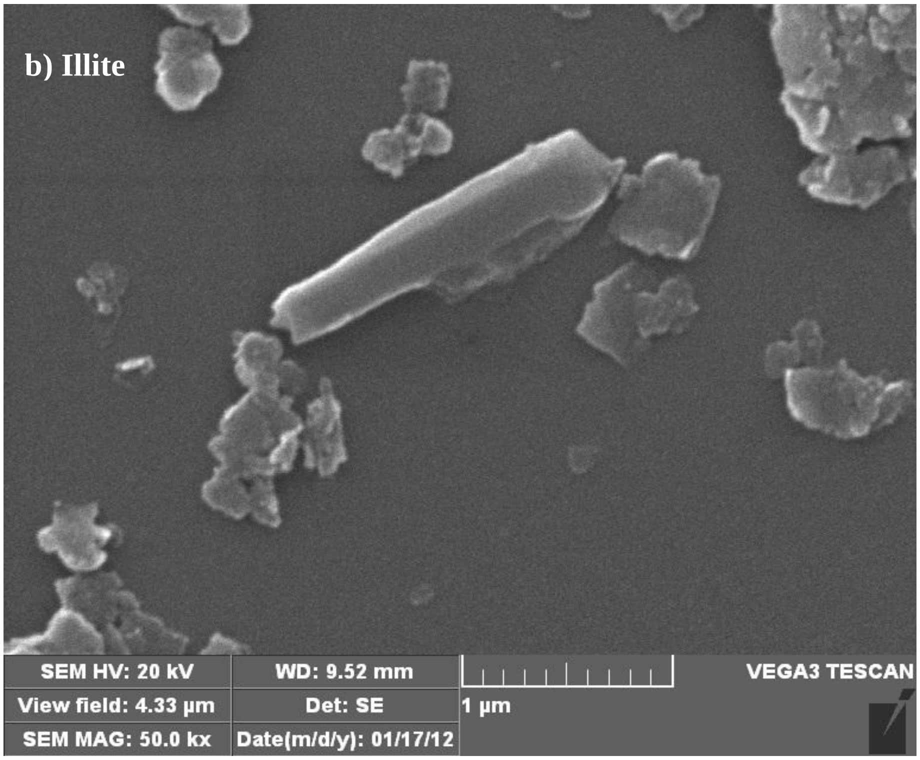


Figure 5-6 Probability of coalescence for emulsions with different types of solids

Treated kaolinite, siderite and silica particles proved good stabilizers of water droplets in oil with a low probability of coalescence. However, treated illite offered little resistance to droplet coalescence with over 90% probability of coalescence. Most of water droplets in presence of treated illite coalesced so the emulsion was not very stable and water phase and oil phase completely separated within 5 days. On the other hand, treated siderite formed the most stable emulsion since it had lowest value of probability of coalescence. In fact, treated illite and treated siderite acted differently in the emulsion whereas their contact angle values were almost similar. It can be concluded that the hydrophobicity of a solid is not the only factor in emulsion stabilization.





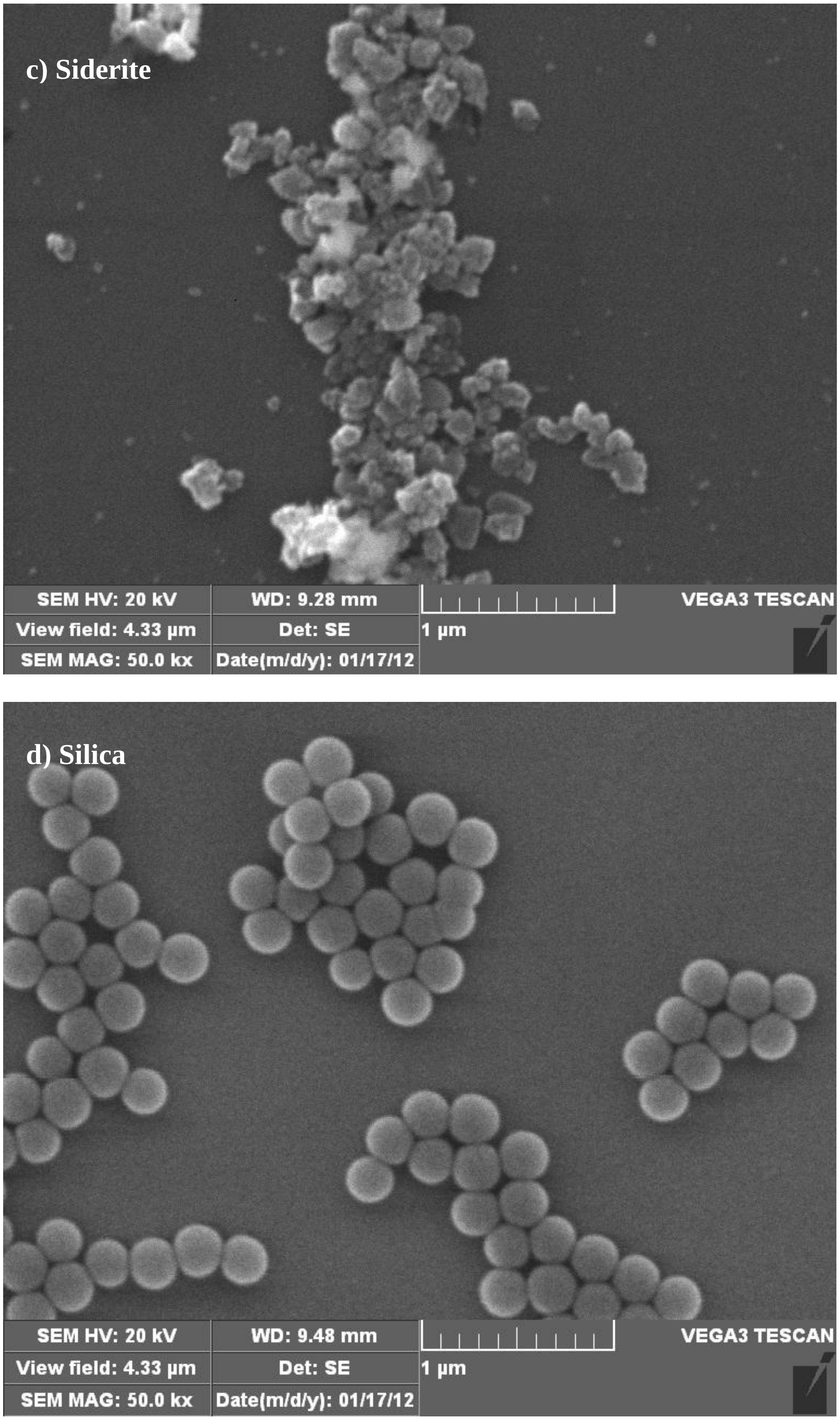


Figure 5-7 SEM images for a) kaolinite, b) illite, c) siderite and d) silica

The scanning electron microscope reveals the shape of each solid to some extent. SEM images of the four types of solids are shown in Figure 5-7. Kaolinite particles had a plate like shape. As previously stated [16], kaolinite has the lowest aspect ratio and is the most spherical clay, while illite has the highest aspect ratio observed to be elongated or very thin. High aspect ratio of illite may support the high probability of coalescence since the particle coverage may be extremely porous. Siderite had irregular shape and silica was spherical. Thus considering their contact angle, they would be expected to form efficient interfacial stabilizers.

5.4 Solid content

In oil sands processing where there is abundance of fines in the ore, high volume emulsions often form resulting in reduced throughput. To understand the effect of solid particle concentration on emulsion stability in diluted bitumen-water system, five emulsion samples with different solid concentrations were prepared. T-K-105 was used in this set of experiments since the solids were previously shown to stabilize water droplets in oil, see section 5.2.

Five emulsion samples were prepared using DI water as an aqueous phase and 33 wt% toluene diluted bitumen as an oil phase with same ratios as mentioned in section 5.1.2. A controlled experiment including no solids with a further four samples containing 0.5, 1, 2 and 5 g/L of T-K-105 solid. It should be noted that all solids were dry prior to addition during mixing. Since the bitumen content was high, micropipette technique was used to evaluate emulsion stability. Figure 5-8 illustrates the probability of coalescence for each sample.

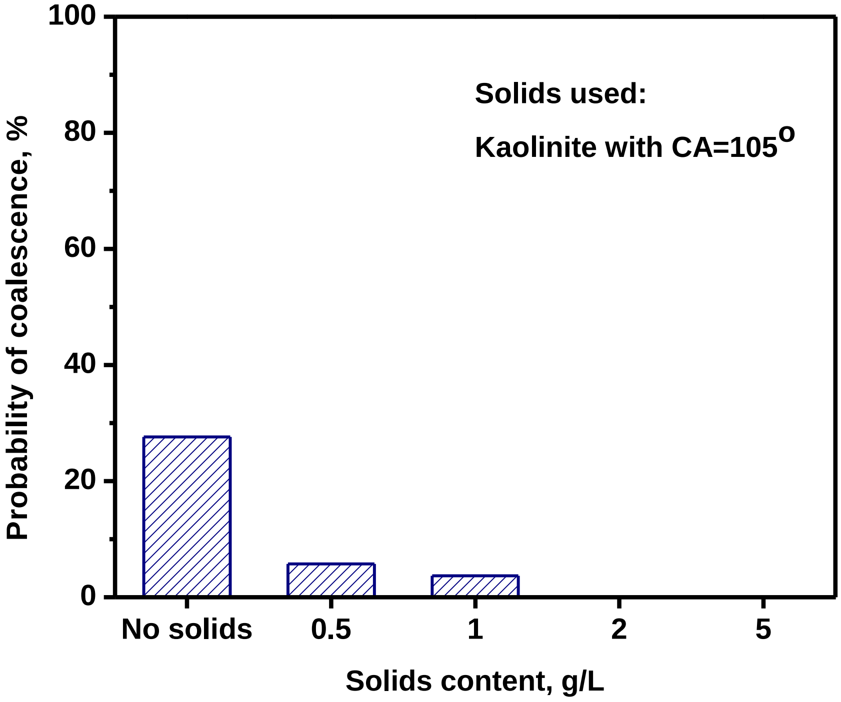


Figure 5-8 Probability of coalescence for emulsions with different solids content

By comparing the first two data set in Figure 5-8, control and the sample with 0.5 g/L solid addition, it can be concluded that small amount of hydrophobically modified solids can increase emulsion stability dramatically. At 2 and 5 g/L the probability of coalescence equaled 0, most likely due to the solids providing complete interfacial coverage.

5.5 Solid size

As previously shown in section 4.2.2 original and ground kaolinite adsorbed similar amount of hydrocarbons from diluted bitumen on their surface and their contact angles were very close. The only difference between these two samples was their particle size. The d_{50} measured for original kaolinite is 4.5 µm, which was more than 30 times larger than ground kaolinite with d_{50} of 130 nm.

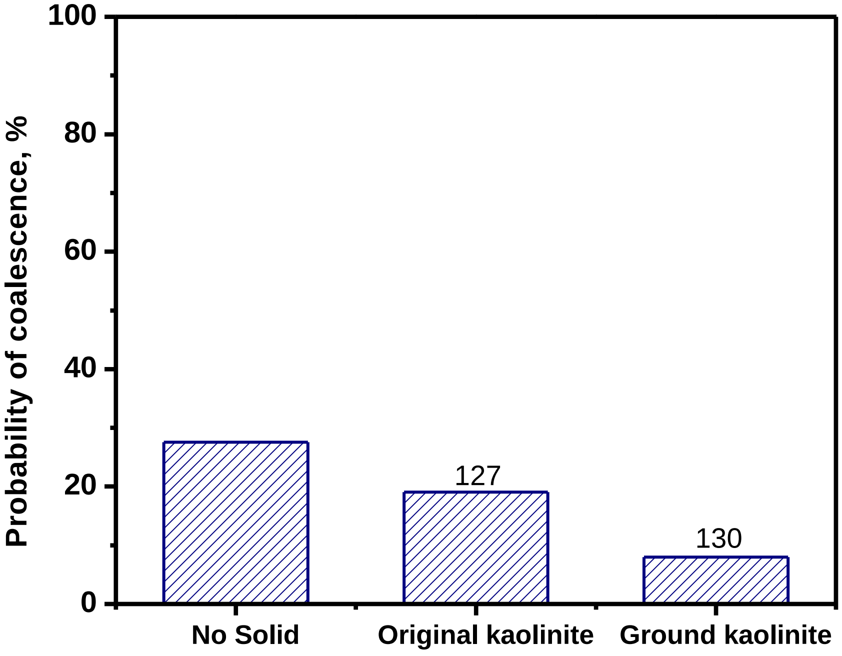


Figure 5-9 Probability of coalescence for emulsions with different solid sizes

To study the effect of particle size, three emulsion samples were prepared. The first sample remained the control (no particles) with two more samples containing original treated kaolinite and ground treated kaolinite. Emulsion preparation procedure was performed at 33 wt% bitumen content as described in 5.1.2. once the emulsion had settled to a steady state, 50 µL of the emulsion was taken and diluted with 10 mL toluene to study water droplet coalescence using micropipette technique.

The probability of coalescence for all three samples is shown in Figure 5-9. Even though the original particles were 4.5 µm, they reduced the probability of coalescence slightly which suggests that the particle position at the interface and hinder the coalescence event. For the ground particles of similar hydrophobicity the probability of coalescence reduced further from 20% for original treated kaolinite to about 8% for ground treated kaolinite. This reduction is expected when you consider the coverage efficiency of nanoparticles.

5.6 Effect of water fraction at a given solid hydrophobicity

The water: oil ratio can also affect the type of emulsion formed. In surfactant stabilized emulsions, an increase in volume percentage of one phase would change the continuous phase of the emulsion. This type of conversion is also known as catastrophic inversion [48].To investigate the effect of water fraction (ϕ_w) on type of emulsion in presence of solids, six emulsion samples were prepared using 1 g/L of dry treated kaolinite with contact angle of 105°. Oil phase bitumen content for all samples was fixed at 10 wt% but the volume percentage of aqueous phase varied from 10 vol% to 90 vol% in six samples. It should be noted that T-K-105 was added as a dry powder while oil phase and water phase were mixing. Prepared emulsions were transferred to graduated cylinders and left until there was no significant change in the volume of partitioned phases.

The volume of emulsion phase for each case was recorded after 20 hours and is illustrated in Figure 5-10. Emulsion type was determined by the addition of one drop of emulsion into either toluene or water. The phase in which the droplet dissolve was considered as the continuous phase.

At water fraction less than 60 vol% all the emulsions were oil continuous (water-in-oil). However, at water fractions greater than 60 vol% the emulsions were observed to invert, forming a water continuous emulsion. The figure also shows that as the ratio approaches the inversion point, the volume of emulsion decreases, forming almost no emulsion at the inversion point.

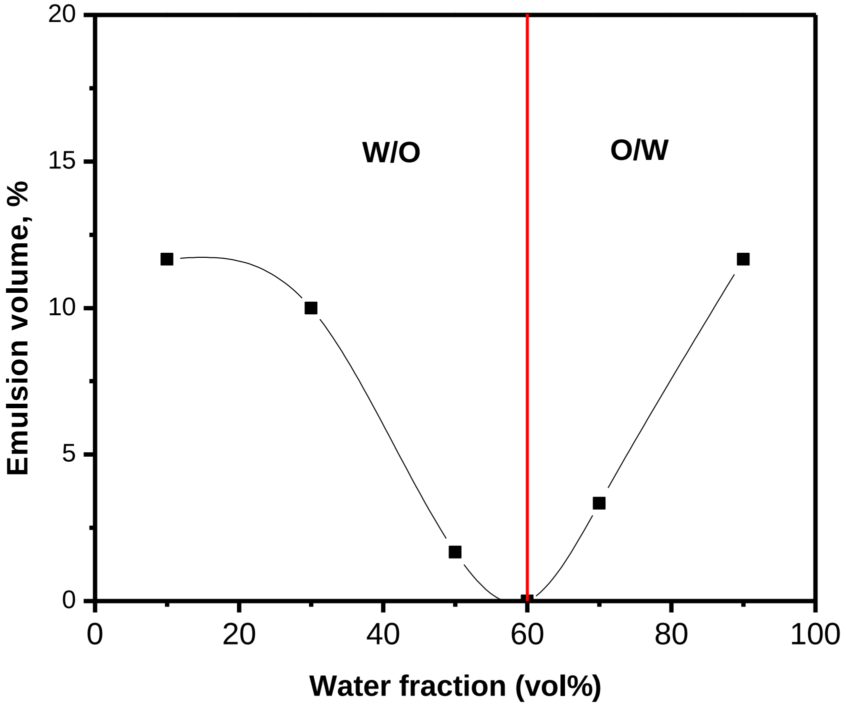


Figure 5-10 Type of emulsion and volume for six water fractions

To determine the size of droplets formed in each emulsion an optical microscope was used. 10 images were taken of each sample and the diameter (water or oil) of at least 50 droplets was measured. The d_{50} for each emulsion is presented in Figure 5-11.

At a given solid content and solid type, by changing the water: oil volume ratio, the emulsion droplets reach a size governed by a dynamic balance between droplet coalescence and break-up. From 10 vol% to 50 vol%, increase in the water volume fraction leads to an increase in the water droplet diameter. After certain ϕ_w, the emulsion converts from w/o to o/w (ϕ_w^{inv}). Then by addition of more water, oil droplets formed and their size decreased in 90 vol% water.

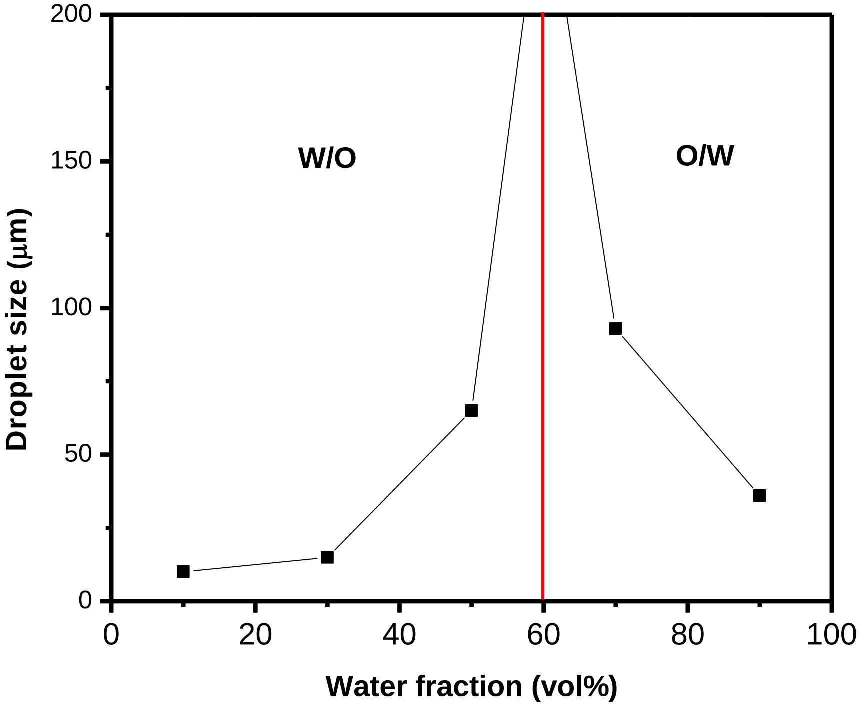


Figure 5-11 The median droplet size in different water fractions

Comparing the size of water droplets at 30 vol% or 50 vol% to oil drops at 70 vol% or 90 vol% showed that water droplets are slightly smaller or in other words the emulsion is more stable as w/o form than as o/w form. This behavior is understandable since T-K-105 is slightly hydrophobic and favors oil continuous emulsions.

ϕ_w^{inv} for treated kaolinite with contact angle of 105° was measured about 0.6, which means at 60 vol% water the emulsion stabilized by T-K-105 converts from water-in-oil to oil-in-water. Same type of experiment was performed for other samples of treated kaolinite of different hydrophobicities to investigate the effect of contact angle on ϕ_w^{inv}. The results are shown in Figure 5-12.

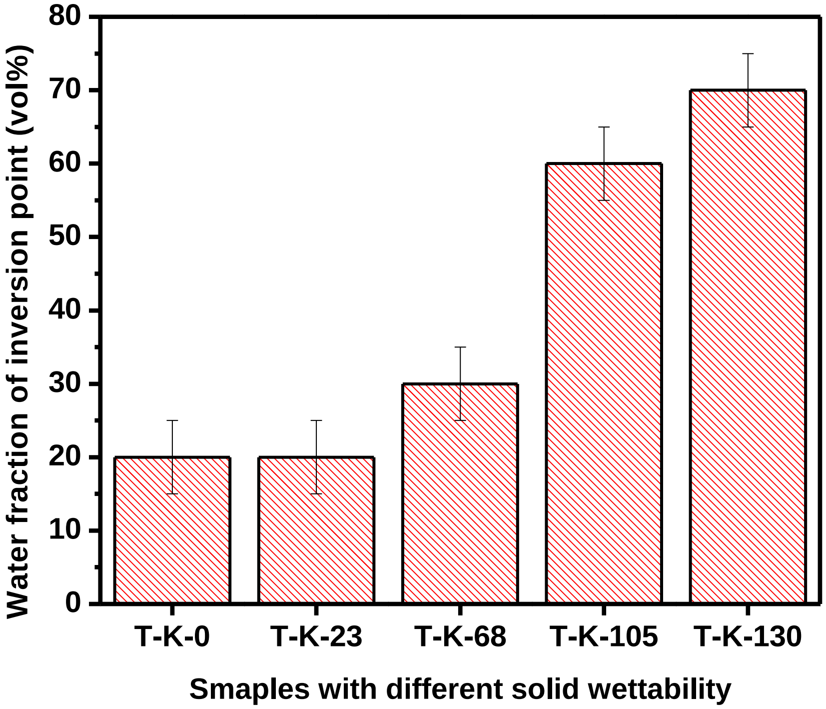


Figure 5-12 Water fraction of inversion point for treated kaolinite with different hydrophobicities

Figure 5-12 shows that as the contact angle increased from 0° to 130° the water fraction at the inversion point also increased from 20 vol% to about 70 vol%, which means that as the particles become more hydrophobic their tolerance to stabilize water droplets in oil phase increases. For example, at 50 vol% water T-K-105 and T-K-130 would form water-in-oil emulsion. However T-K-0, T-K-23 and T-K-68 would have already inverted the emulsion and formed oil-in-water emulsion.

5.7 First phase dispersion-Initial particle location

Initial location of solid particles may affect the type of emulsion and stability because it can change the surface properties of solids. In all experiments presented in this part, the dry solids were added while oil phase and aqueous phase were mixing together. To study the possible effect of initial location of solids on emulsion, five pairs of emulsions in different water fractions were formed. Each pair was prepared as followed:

In the first sample, solids were sonicated in water for 10 minutes then the oil phase was added and mixed using a homogenizer. In the second sample, solids were placed in the oil phase and sonicated for the same duration then water was added and mixed. The emulsions were compared in each case. This experiment was performed at five water fractions of 10, 30, 60, 70 and 90 vol% using DI water as an aqueous phase and 10 wt% diluted bitumen as an oil phase. The solid that was used in all samples was treated kaolinite with contact angle of 105°.

At 10, 30, 70 and 90 vol% water fraction:

Although the initial phase that T-K-105 was first dispersed in was different for each pair(water phase as the first sample and oil phase as the second sample), there was no significant difference between the emulsions that were formed at same water fraction.

At 60 vol% water fraction:

In the first sample where solids were dispersed in water, 1.2 mL of o/w emulsion formed. However in the second sample, where the T-K-105 was dispersed in oil phase, almost no emulsion formed.

From Figure 5-13 it is possible to compare water fractions of inversion point for three systems that were prepared using T-K-105. The first bar refers to the system that solid samples were first placed in water and then the oil phase was added. In this way, at 40 vol% water, the emulsion inverted from o/w to w/o therefore ϕ_w^{inv}= 40%. In the second system, where T-K-105 was first dispersed in oil, water fraction of inversion point was measured to be about 60%. The third bar shows the ϕ_w^{inv}=60% for the system in which the solids were added as dry powder to the mixing oil and water system.

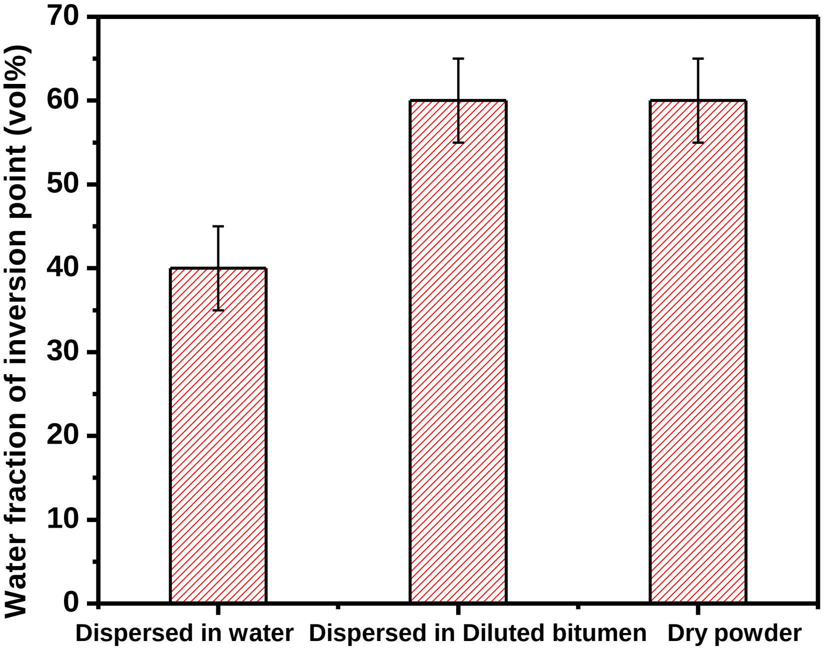


Figure 5-13 Water fraction of inversion for T-K-105 initially dispersed in oil or water phase

Therefore, it can be concluded that:

- The initial location of solids affects ϕ_w^{inv} of T-K-105.
- Dispersion of T-K-105 in the oil phase was very similar to the addition of dry powder to oil-water mixture. This confirms that the solids preferred the oil phase when they were added as a powder to the mixing oil-water system because the solids are hydrophobic.
- As a bi-wettable solid if T-K-105 was first dispersed in aqueous phase it would form oil-in-water emulsion at low water fraction. In other words, dispersion of this solid in water would change the in-situ contact angle and reduce the solid hydrophobicity and that was why ϕ_w^{inv} decreased to 40 vol%.

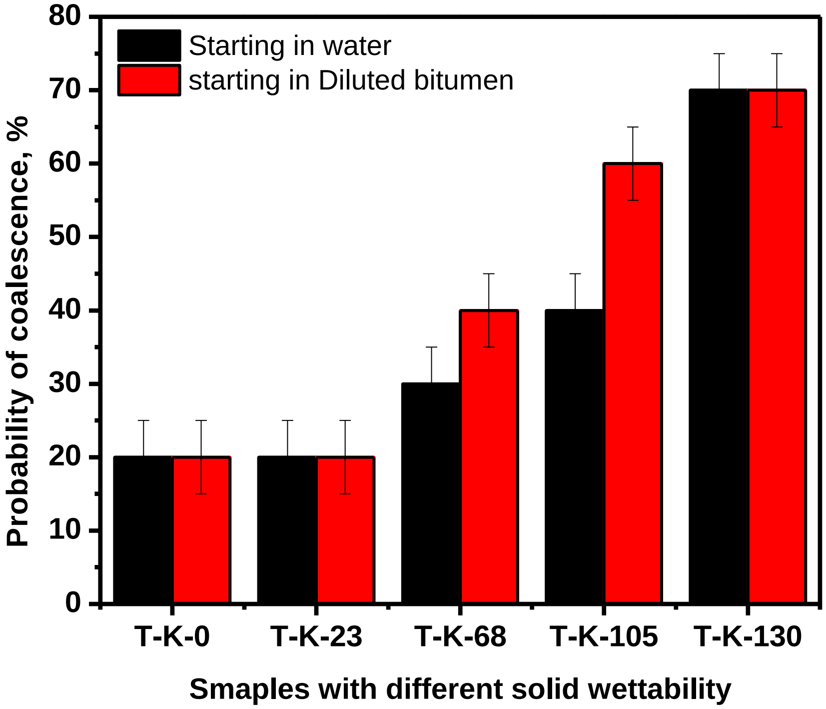


Figure 5-14 Water fraction of inversion point for treated kaolinite with different hydrophobicities based on initial location of solids

Figure 5-14 compares ϕ_w^{inv} for all treated kaolinite samples based on the initial location of solids. For T-K-130, T-K-23 and T-K-0 there is no dependency on the dispersion phase. So it can be concluded that if the solids are very hydrophobic or hydrophilic they would not be affected by their dispersion location. For example, dispersing T-K-130 in water did not change the in-situ hydrophobicity of this solid sample, thus ϕ_w^{inv} remained 70 vol%. On the other hand, bi-wettable solids like T-K-105 and T-K-68 had different ϕ_w^{inv} when they were placed in different phases. It should be noted that, from Figure 5-12 the ϕ_w^{inv} of T-K-68 was 30 vol% for the dry powder sample which is similar to the value of water dispersed sample. In fact, treated kaolinite with contact angle of 68° preferred the aqueous phase even when it was dry. Addition of T-K-68 first to the oil phase caused an increase in in-situ contact angle and it enhanced the water fraction of inversion point for this solid from 30 vol% to 40 vol%.

5.8 Water pH

In all previous cases, DI water was used as the aqueous phase. Changes in water phase chemistry may affect the water-oil interfacial properties. To study the effect of pH on emulsion stability four emulsion samples were prepared using T-K-105 and 10 wt% diluted bitumen as the oil phase. The samples contained 30 vol% aqueous phase at four different pH values of 4.1, 6.2, 9.6 and 11. Each emulsion was prepared by mixing 8.4 mL oil phase and 3.6 mL of aqueous phase in a 20 mL vial and addition of 1 g/L of dry powder T-K-105. Samples were mixed for 5 minutes at 13000 rpm. The emulsion volumes were recorded after 20 hours once there was no significant change in the volume of partitioned phases.

As shown in Figure 5-15, at pH 4.1 the emulsion volume is less than 2% while at pH 11 emulsion volume increased to about 50%. This significant increase in stability clearly demonstrates the role of pH on emulsion stability. This phenomenon can be explained by two reasons:

- Increase in pH results in increase in surface active components in the system. For example at high pH, naphthenic acids in bitumen would ionize and naphthenate forms, which is surface active and can stabilize water droplets [2].
- At high pH, zeta potential of treated kaolinite would decrease. Therefore, the solids covered water droplets could disperse better due to repulsive force formed as a result of negative charge on the surface of particles. Therefore, the emulsion becomes more stable.

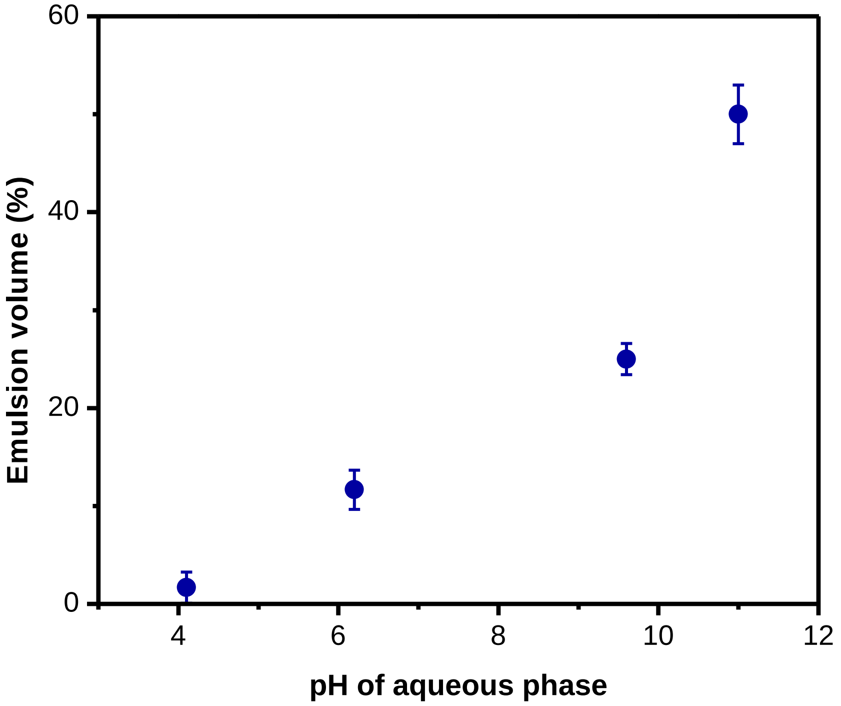


Figure 5-15 Effect of pH on emulsion volume

5.9 Multiple emulsion

As previously stated, in separation vessels of froth treatment process, emulsions build up between oil and water phases reducing dewatering capacity and influencing bitumen recovery. These emulsions may not be simple oil-in-water or water-in-oil emulsion. In fact in many cases such as rag layer, complex emulsions are often observed. Multiple emulsions form where one water droplet is trapped inside another oil droplet in a water phase or vice versa. Solids with different hydrophobicities can play important role to form these complex emulsions. To investigate the formation mechanism of multiple emulsions, T-K-105 and T-K-68 were used as the solid samples.

The emulsion preparation procedure was completed in two stages. For oil/water/oil emulsion, first T-K-68 as a hydrophilic solid was mixed at 13000 rpm with 6 mL water and 6 mL of 10 wt% diluted bitumen. Therefore, oil-in-water emulsion was formed. Then T-K-105 and another 6 mL oil phase were mixed with previous mixture at 6000 rpm. The reason for reducing the speed at the second stage is not to break the previous oil-in-water emulsion. The image shown in Figure 5-16 clearly shows oil drops are trapped in water droplets in a continuous oil phase. Treated kaolinite solids with contact angle 105° stabilized water droplets in the oil phase (outer surface) and T-K-68 stabilized oil drops inside the water droplets.

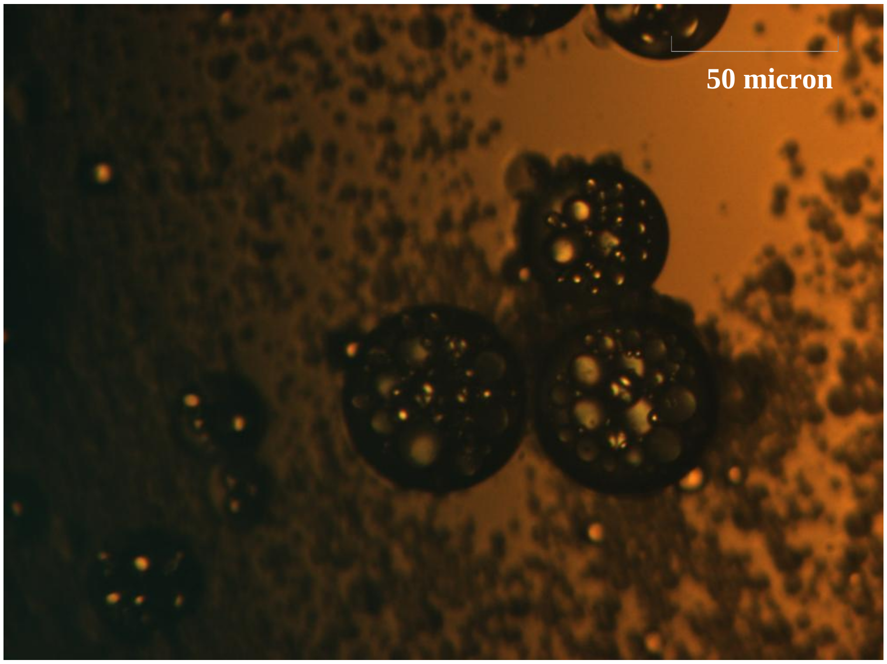


Figure 5-16 Oil/water/oil emulsion

To form water/oil/water emulsion the same procedure can be used when lowering the bitumen content in the oil phase. Also, the T-K-105 as the hydrophobic solid should be added in the first part and T-K-68 the hydrophilic solid was added in the second part. Figure 5-17 shows water droplets in oil drops in a water continuous water phase. Here T-K-105 covered the inner surface and formed water in oil emulsion and T-K-68 stabilized oil drops in water. Therefore, presence of two types of solid particles, one hydrophobic and one hydrophilic in oil sands can lead to formation of multiple emulsions. This mechanism could help explain rag layer formation in separation vessels.

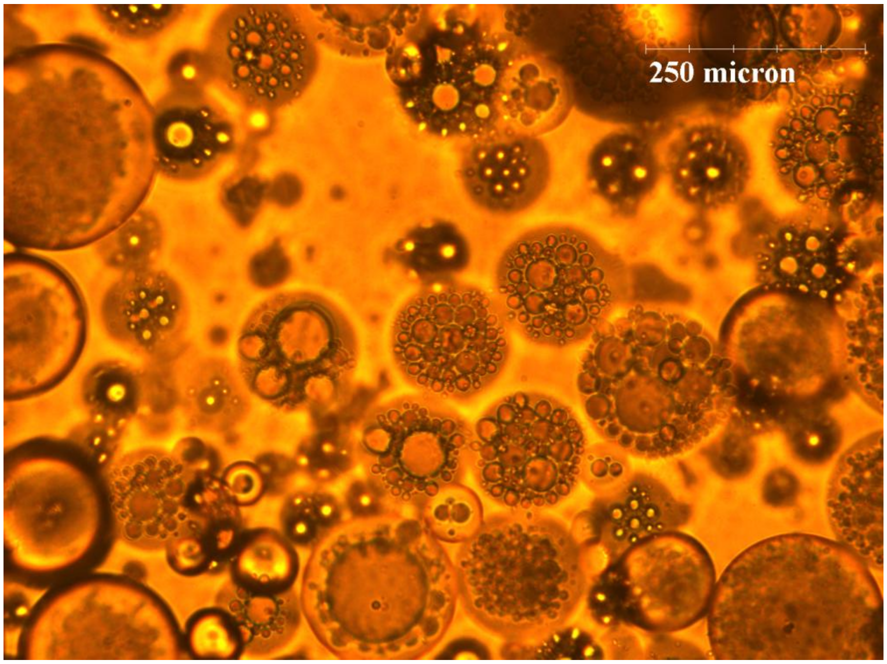


Figure 5-17 Water/oil/water emulsion

5.10 Summary

In this chapter the study focused on emulsion stability as a function of treated solid samples that were prepared and characterized in chapter 4. Results showed that bitumen addition would increase emulsion volume. At low bitumen content hydrophilic solids formed high volume of oil-in-water emulsion and in between the emulsion of T-K-68 held the highest emulsion stability. At high bitumen content, water in oil emulsion formed and the emulsion stability was studied under the effect of the following factors:

- Effect of solid hydrophobicity:

Treated kaolinite with contact angle of 105° formed the most stable emulsion compared to other solid samples although T-K-130 also stabilized water droplets very well. Therefore hydrophobic solids were favorable for w/o emulsions.

- Effect of solid type:

Micropipette test of emulsions formed by 4 types of solids showed that, treated illite destabilized the emulsion in contrast to treated kaolinite, siderite and silica that stabilized water droplets in diluted bitumen. The shape of solid could be the reason for the difference in emulsion stability.

- Effect of solid content:

Addition of slight amount of solids to the oil-water mixture considerably changed the stability of water droplets. Increase in solid concentration to 2 g/L led to zero probability of coalescence of emulsified water droplets.

- Effect of solid size:

Comparison of ground and original treated kaolinite showed that fine solids have stronger ability to stabilize water in oil emulsion than coarse solids.

Also the change of water fraction in the system showed that for all treated kaolinite samples there is a water fraction at which the emulsion converts from water-in-oil to oil-in-water (ϕ_w^{inv}). Increase in hydrophobicity of solid sample led to higher value of ϕ_w^{inv}. Besides, initial dispersion of solids in either aqueous or oil phase would change the ϕ_w^{inv} in the case of bi-wettable solids T-K-105 and T-K-68.

It was also shown that increase in pH of water resulted in higher volume of emulsion at a given solid type and solid content. Also, applying two types of solids, one hydrophilic and one hydrophobic resulted in formation of multiple emulsions.

6 Conclusion and future work

6.1 Overall conclusions

The effect of solids on the emulsion formation in water-diluted bitumen system was investigated.

For the first part of the study, four types of solids, kaolinite, illite, siderite and silica, were prepared by exposure to toluene diluted-bitumen and to study the adsorption of organic compounds on their surface. Such prepared solids had varying wettability. The following factors were studied during sample preparation:

Solid type: All samples were contaminated during the treatment process by diluted bitumen. However kaolinite affinity to bitumen components was higher than 3 other types of solids.

Solid size: Comparison between treated original kaolinite and treated ground kaolinite showed that size could not affect the organic adsorption process.

Water film around solid particles: The water film around the kaolinite particles acted as a shield and prevented the organic adsorption on clay surface; therefore the wetted sample remained hydrophilic.

Bitumen concentration: Increasing concentration of bitumen in diluted bitumen solution enhanced the contamination on kaolinite surface. Therefore a range of clay hydrophobicities including hydrophilic, bi-wettable and hydrophobic solids were formed.

Later the emulsion formation and its stability as a function of oil phase, aqueous phase and properties of solid samples were studied. Results showed that increasing bitumen concentration in the oil phase would increase the emulsion volume. At low bitumen content hydrophilic solids stabilized high volume of oil in water emulsion compared to hydrophobic kaolinite samples. Four series of emulsion prepared at high bitumen content to study the effect of solids.

Solid hydrophobicity: hydrophobic treated kaolinite stabilized water in oil emulsions better than hydrophilic samples. In between, the solid with closer contact angle value to 90° formed the most stable emulsion.

Solid type: Micropipette tests for emulsions showed that treated illite could not stabilize water droplets in the emulsion very well compared to treated kaolinite, siderite and silica.

Solid content: Higher solid concentration in the emulsions reduced the probability of coalescence since higher concentration of treated kaolinite particles could better cover the water droplets and prevent the droplets coalescence.

Solid size: Although the particle size had no effect on organic adsorption, treated ground kaolinite stabilized the emulsion better than treated original kaolinite. Therefore the finer the solids are the more stable the emulsion would be.

Increasing the water fraction at the given solid type and solid content inverted the emulsion from water in oil to oil in water. The water fraction at which the emulsion inverted (ϕ_w^{inv}) increased by using treated kaolinite particles of higher hydrophobicity. It should be also noted that the ϕ_w^{inv} depended on initial location of particles only if they were bi-wettable. Further experiments showed that, increase in pH of water resulted in higher volume of emulsion due to the change in particles surface charge and higher concentration of surfactants in the system. Besides, by addition of two samples of treated kaolinite, one slightly hydrophilic and slightly one hydrophobic to the water-diluted bitumen system multiple emulsions formed.

6.2 Suggested future work

This work showed that presence of solids with two different hydrophobicities resulted in formation of multiple emulsions. Considering that multiple emulsions such as rag layer in separation vessels hinder the oil and water separation process, it would be expedient to perform a systematic study on the emulsions formed by mixture of particles with different hydrophobicity.

Furthermore, asphaltenes were stated to be the main compounds adsorbed on clays [34]. In this work adsorption of all bitumen components was presented. It would be useful to study adsorption mechanism of asphaltenes free-bitumen on solids surface.

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