University of Alberta

Characterization of Fine Solids in Bitumen Froth Before and After Hydrothermal Reactions

By

Jun Zhao

A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of

Master of Science

in

Chemical Engineering

Department of Chemical and Materials Engineering

Fall 2013
Edmonton, Alberta

ABSTRACT

In this study, the mineralogy, surface properties, and morphology of fine solids in bitumen froth before and after hydrothermal reactions were investigated. It was observed that clay minerals such as kaolinite and illite did not go through significant mineralogical changes after the reaction. However, the siderite and pyrite contained in the bitumen froth were found to convert to pyrrhotite after the reaction. This conversion could be advantageous during direct hydrothermal froth upgrading as it fixes sulfur. The fine solids in bitumen froth were found to possess diverse wettability but they turned uniformly more oil-wet. Consequently, the fine solids lost their emulsion stabilization function as they mostly stayed in the oil phase. The filterability of the fine solids in the bitumen froth was also significantly increased, possibly due to a change in wettability and particle size. Therefore, hydrothermal reactions of bitumen froth can destabilize water-in-oil emulsions and facilitate fine solids removal.

ACKNOWLEDGEMENT

Firstly, I would thank my supervisor Dr. Murray Gray and Dr. Qi Liu for their thoughtful guidance and sincere suggestions. I am grateful to them because the two years graduate study is truly enjoyable experience and I gained useful knowledge for my future career.

Secondly, I would thank Xiaoli Tan, Keith Draganiuk, Lisa Brandt, Jeremiah Bryksa, Dimitre Karpuzov, Shihong Xu, Anqiang He, Bojia Zhang for their technical support. Their support on sample ordering, instrumental instruction, and technical trouble shooting is greatly appreciated.

Special thanks to Igor Stricek and Peiwen Wang for their cooperation during this study. I am appreciated for the X-Ray Diffraction technical support from Igor and Kaolinite model system done by Peiwen Wang.

I am grateful for the financial support of National Sciences and Engineering Research Council of Canada (NSERC) and Imperial Oil.

Lastly, I would thank my parents for their support and encouragement. No matter how tough life becomes, they will always be a powerful and secure backing.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER ONE
INTRODUCTION

1.1 Introduction

In northern Alberta, there are large amounts of oil sands deposits. The recovered oil from oil sand is named bitumen and is very heavy compared to conventional crude oil. The total oil is estimated to be more than all OPEC reserves combined (Chen et al., 1999), and about 180 billion barrels of bitumen that can be recovered with current technology. Unlike conventional crude oil, the oil is intermixed with sands. Thus, a separation process is necessary. In addition, bitumen has much lower hydrogen content and higher undesirable elements such as sulfur and metal than conventional crude oil. Bitumen separated from oil sands is also very difficult to transport because it has very high viscosity. Therefore, upgrading processes are necessary to make bitumen as valuable as light crude oil. The cost to process oil sands can be as high as 60-90 US dollars/Barrel (Sreekumar, 2013) because of those extra processes. However, due to the depletion of conventional crude oil, the oil sands industry brings more and more investment.

For those shallow oil sands ores usually mined by open pit mining, followed by a widely employed oil sands extraction technology called aqueous extraction. The process takes place in warm water (~50°C), At pH of about 8.5, bitumen attached to sand grains is liberated and detached from the sand grains. Once air is introduced, most bitumen will attach to the air bubble and then float on top of the water layer. Meanwhile, some fines, which are some mineral particles normally smaller than 44μm, also attach to the liberated bitumen and air bubbles. With large sand grains removed, the liberated bitumen is collected. It still contains significant amount of fines and water, so it is called bitumen froth. Typical bitumen froth from northern Alberta contains about 80-85 wt% of bitumen, 10-15 wt% water, 5-10 wt% fine minerals. The water and fines are very difficult to remove because water is normally emulsified in the oil phase and the fines contribute to stabilize the emulsion. Those emulsified water droplets carry salts such as NaCl. Even the water is removed by heating the bitumen froth, those salts still stay in the bitumen and cause corrosion issues in the downstream equipment. Furthermore, the appearance of fine solids can cause equipment fouling (Masliyah et al., 2011). Therefore, currently froth treatment is used to remove the fines and water prior to bitumen upgrading. Froth treatment mainly is adding diluents to reduce the viscosity of bitumen froth so that fines and water droplets can be centrifuged out. There are two types of diluents currently being used. One is paraffinic diluents such as hexane. After adding paraffinic diluents, fines, water droplets, and asphaltene flocculate to form flocs so that they can be easily removed (Dabros et al., 2004). Asphaltene is the heaviest and most polar portion of bitumen that does not dissolve in paraffinic solvents but is soluble in toluene. To remove the fines and water, about 7% of total bitumen needs to be discarded in the form of asphaltene during this type of froth treatment. The other diluent is naphtha, which can be produced in the downstream during bitumen processing. Adding naphtha to froth will not precipitate asphaltene, fines and water will not flocculate as efficiently as if paraffinic diluent is used, hence the treated bitumen is not as clean. Both methods can cause environmental issues due to residual diluent in the tailing water, and extra energy is needed to recover the diluents.

Improvement of froth treatment can be beneficial. Detailed currently employed froth treatment will be included in literature review section.

A conceptualized technique “froth upgrading” is now being studied in University of Alberta. This technique is intended to combine the froth treatment and upgrading steps in order to produce clean pipelineable product in a single step. The core steps of this technique are first to heat the froth to reaction temperature, and then separate the water and minerals from bitumen. To make the technique feasible, it is necessary to understand how bitumen, water and minerals interact with each other under hydrothermal reaction conditions. A hydrothermal reaction condition is reaction that involves water at elevated temperature and pressure. Sōmiya et al (1995) stated that hydrothermal condition is between 100°C and 1800°C and the pressure should range from 0.1-1500MPa. In this study, the reaction temperature will be in the range of 400-440°C. Due to industrial limitations (e.g. high cost to build very high pressure reactors), the pressure of interest should below 13MPa and the residence time should be in the range of half hour to two hours. At this moment, studies are mainly focused hydrothermal reaction of bitumen froth produced by hot water extraction.

1.2 Objectives

The main objective is to study the effects of hydrothermal reaction under near-supercritical conditions on the fine solids in bitumen froth. The following research questions will be investigated:

- How do hydrothermal conditions change the mineralogical composition of the fines?
- What are the amounts and the types of organics associated with the fines before and after reaction? For example, sulfur analysis can provide information about sulfur removal due to reactions of minerals.
- What are the surface properties of the fines, especially the wettability alteration during reaction? Valuable information can be gained from these results about how difficult the minerals are to remove after the reaction.
- How are the morphology and particle size of the fines altered, and how does the filterability change?

CHAPTER TWO
LITERATURE REVIEW

2.1 Oil Sand Mineralogy

Alberta oil sands contain 55–80% minerals, 4–18% bitumen, and 2–15% water (Kasperski, 2001). The minerals are predominantly Quartz, with a size range larger than 44µm. Those sand grains are easy to remove. According to Hepler and Smith, a typical sample of Alberta oil sand contains about 82% Quartz, 5% feldspar, and trace of siderite, pyrite, and Calcite etc. However, the majority of the quartz and feldspar in oil sands have particle size larger than 250µm. Once only the fines in froth are considered. The percentage of quartz significantly decreased. Fine solids that are smaller than 44µm are much harder to remove. They are much more problematic due to their tendency to stabilize emulsions. Fine content is commonly a descriptor of oil sands quality. High-fine ore contains more than 18% fines and low-fine ore normally contains less than 6% of fines (Kasperski, 2001). In the following sections, the main components of these fine solids are discussed.

2.1.1 Fine Solids in Oil Sands

In the oil sands industry, the fine solids or fines are the fine-grained minerals with particle size smaller than 44µm. The majority of the fine particles in oil sands are clay minerals. The characteristics and properties of fine particles in oil sands are actually determined by all these components (Grim, 1953). In this study, it is necessary to look at those components individually. Due to their high surface area and charge density, they generate negative effects in the oil sand processes. For example, in froth treatment clay particles coated with asphaltene can form barriers around water droplets so that those water droplets will not coalesce hence a water in oil emulsion can be stabilized (Sparks et al, 2003).

The term "clay mineral" refers to “phyllosilicate minerals and to minerals which impart plasticity to clay and which harden upon drying or firing” (Guggenheim, 1995). Kaolinite, illite, chlorite, smectite are the common clays in Alberta oil sands. Among those clays, kaolinite and illite are the most abundant.

2.1.2 Kaolinite

Kaolinite is one of the most common clay minerals in oil sands industry. It consists of 43% the relative amounts of fine solids in a typical sand sample (Kaminsky, 2009). Kaolinite is a typical two—layer clay with Si:Al ratio of 1:1. The Lattice structure is shown in Figure 2.1. A layer of tetrahedral sheet of SiO_2 stack on a layer of dioctahedral aluminas forms a unit layer of kaolinite structure. The interlayers are so narrow that they cannot fit other ions, therefore, this clay will not swell. Thus, the cationic exchange mainly occurs at the edge of the layers.

A common empirical equation for kaolinite is $Al_2Si_2O_5(OH)_4$. However, many other ions can substitute for aluminum or silicon in the structure. For example, silicon can be substituted by aluminum in the tetrahedron sheets or aluminum can be substituted by other compensating ions such as magnesium in the octahedron sheets. Such substitution called isomorphic substitution. The isomorphic substitution can create surface charges, so that cation exchange can occur. For kaolinite, it normally occurs in the tetrahedron sheets and the degree of substitution is relatively small compared to many other clays. Isomorphic substitution breaks the structure homogeneity in clay samples, so that using empirical form may not be always accurate (Masliyah et al., 2011). Kaolinite has high affinity for organic material because of the broken bonds at the edge of the particles and the cation exchange capacity (CEC) from isomorphic substitution near the surface (Lebedeva and Andrew, 2011). Compare to the bitumen in oil sands, kaolinite is much more hydrophilic. The static water sessile drop contact angle of kaolinite powder (<2μm) was measured to be around 20° (Shang et al., 2008).

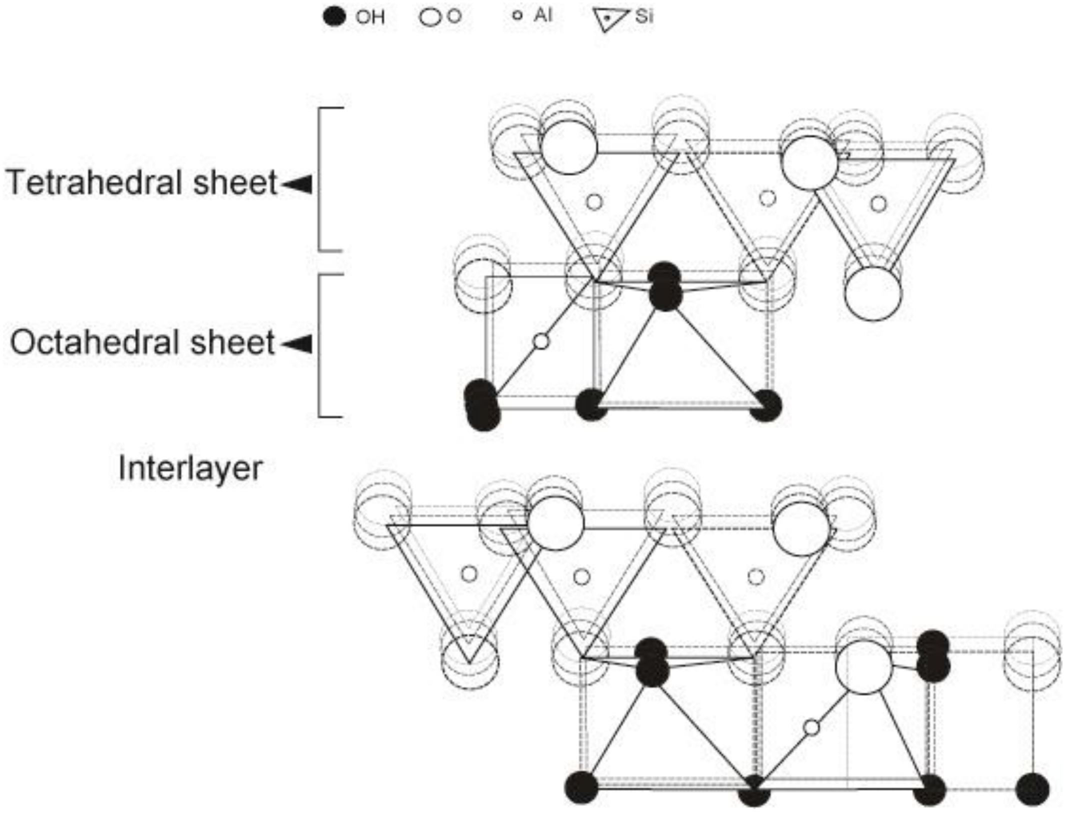


Figure 2.1 Lattice structure of kaolinite (Konan et al., 2007)

2.1.3 Hydrothermal Alteration to Kaolinite

At about 90°C kaolinite starts to lose the adsorbed water to become ‘dried’. If kaolinite is further treated thermally, it may lose the hydroxyl group in its structure. Hydroxyl groups in clay minerals play important role in adsorbing asphaltenes. Details of this will be included in later sections. The reason will be explained in the following sections. Products from dehydoxylation of kaolinite could vary based on the reaction condition and normally, this type of reaction is not reversible. A common product is metakaolin. The possible dehydroxylation of kaolinite needs to be considered in the case of froth upgrading. Hurst and Kunkle plotted the thermal dehydroxylation of Rio Capim kaolinite heated in air. The plot is shown in Figure 2.2. The figure shows that kaolinite will start dehydroxylation when the temperature is above 400°C. At about 450°C, it takes about more than a week for kaolinite to dehydroxylate. However, if the temperature is above 600°C, dehydroxylation becomes very rapid. For froth upgrading, water vapor must be considered and the dehydroxylation of kaolinite in air might not be so useful. The dehydroxylation of kaolinite highly depends on the water vapor pressure (Hurst and Kunkle, 1985). According to Hurst, kaolinite stops dehydroxylating at room temperature if the water vapor pressure is over 3.2 kPa, and at 300°C, 2.8 MPa of water vapor pressure is sufficient to prevent the dehydroxylation. Therefore, they concluded that the dehydroxylation of kaolinite is highly depending on both temperature and water vapor pressure.

Since the reaction conditions in froth upgrading involve near super critical water condition, we need to examine how kaolinite behaves under high temperature and high pressure with the presence of water. Yeskis et al. (1985) put the research findings together and drew a diagram for kaolinite dehydroxylation over the temperature and pressure range of 200—700°C and 0—60 MPa, respectively (Figure 2.3). The results agreed the findings from Hurst and Kunkle (1985) that the higher the water vapor pressure, the higher the temperature required for kaolinite to dehydroxylate in a specific period. Kaolinite started to dehydroxylate at about 300°C if the water vapor pressure is less than 100KPa. It is unlikely that kaolinite will dehydroxylate even at 550°C if the water vapor pressure is greater than five bars. Furthermore, Yeskis found that at about 400°C with the water vapor pressure greater than 80 bars, kaolinite could become pyrophyllite + hydralsite + montmorillonite. However, they stated this reaction process could take weeks to accomplish and in the case of bitumen upgrading residence time, this is unlikely to happen. The above cases are about when kaolinite is the only mineral in the system. At certain elevated temperature up to 265°C, if there are Mg^{2+}, Ca^{2+} or Fe^{2+} in the system, kaolinite can react with quartz to form a swelling clay such as smectite (Bennion and Thomas, 1992). This result implies that under froth upgrading condition, mineral transformations may be very complicated.

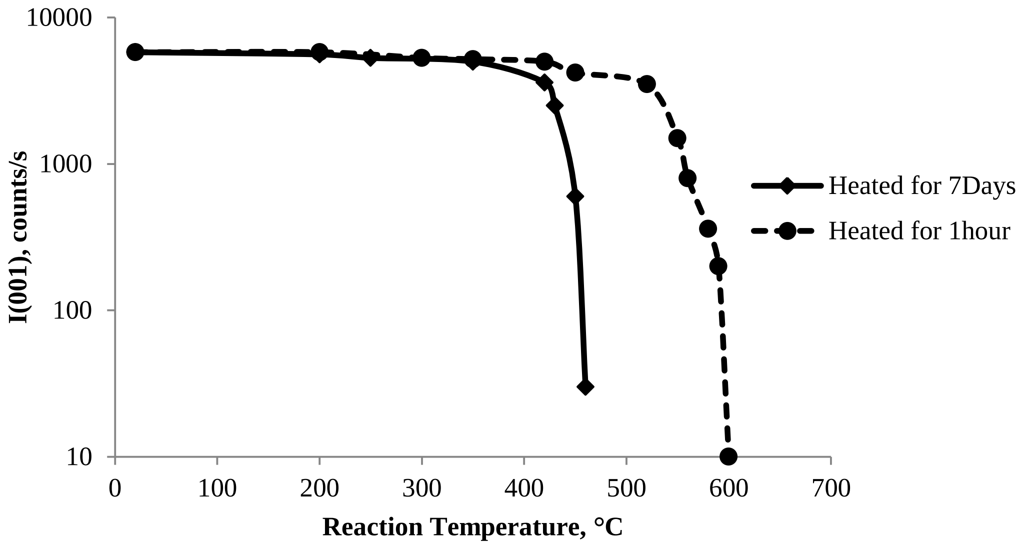


Figure 2.2 Dehydroxylation of Rio Capim kaolinite heated in air based on intensity of the 001 band (I(001)) from X-Ray Diffraction of powder (Hurst and Kunkle, 1985). Each dot represents each sample heated at the temperature showed in X-axis for the amount of time marked in the legendary.

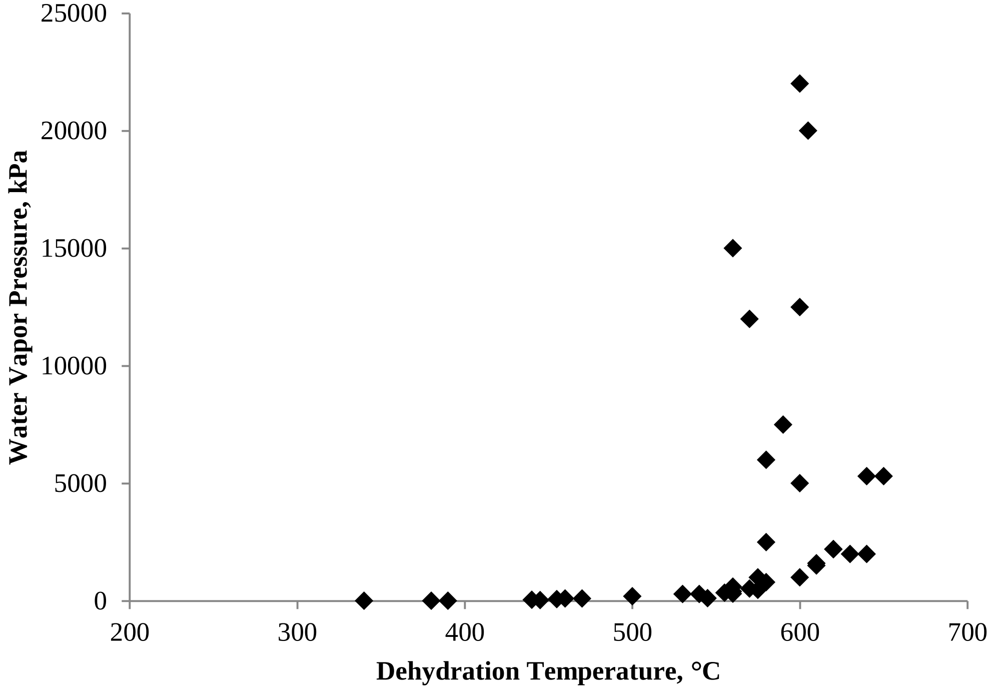


Figure 2.3 Dehydroxylation of kaolinite under hydrothermal conditions (Yeskis, 1985).

2.1.4 Illite

Illite is also very common clay in oil sands. It contributes about 22% of the total clays in oil sands (Kaminsky, 2009). Illite is a three-layer clay mineral with one dioctahedral alumina sheet sandwiched between two SiO_2 tetrahedral sheets (Konan et al., 2007). Differing from kaolinite, the interlayers of illite are commonly occupied by potassium ions, and those potassium ions are not available for cation exchange. The degree of isomorphic substitution in illite is normally much higher than kaolinite, thus, the chemical composition of illite can vary widely. However, an empirical chemical formula of illite is available, which is $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$ (Masliyah et al, 2011). Colloidal illite powders (<2μm) has slightly higher contact angle than kaolinite, which is around 30° (Shang et al., 2008). Compare to bitumen from oil sands, it is very hydrophilic.

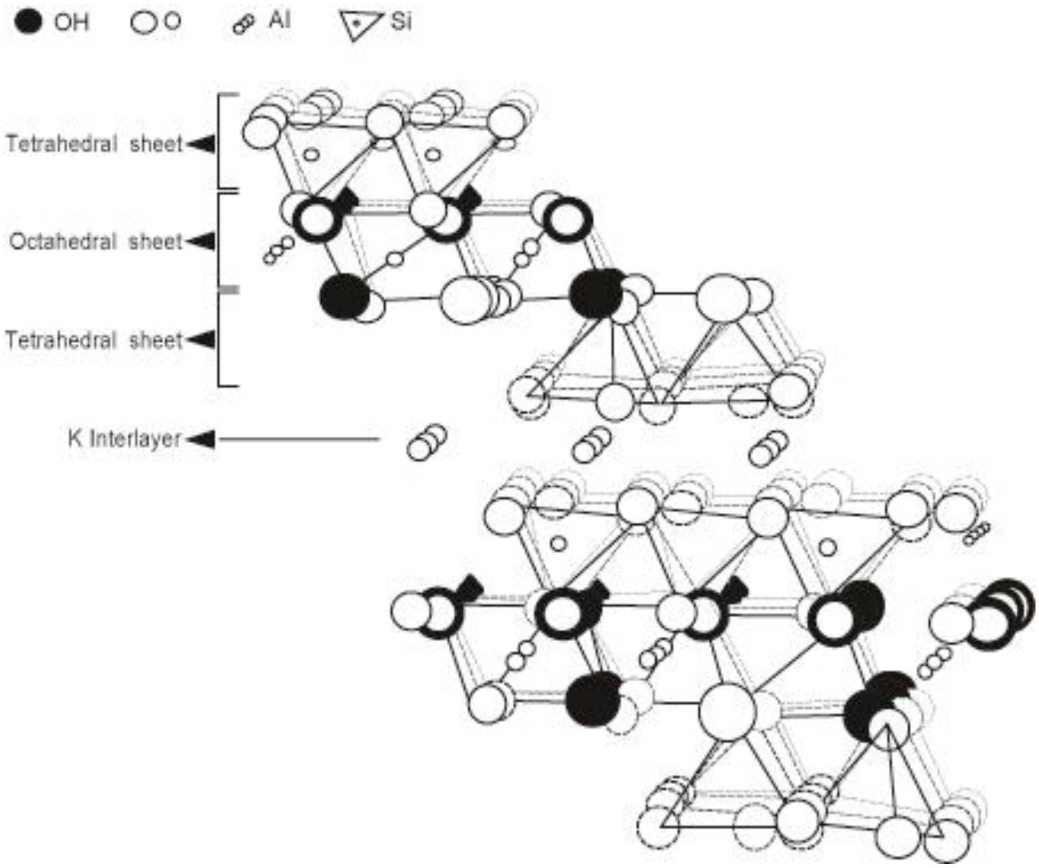


Figure 2.4 Lattice structure of kaolinite (Konan et al., 2007)

2.1.5 Hydrothermal Alteration to Illite

Dehydroxylation could also occur with illite if the temperature is sufficient. The dehydroxylation of illite was first investigated by using different thermal analytical methods such as DTA, TG etc. The onset temperature of the dehydroxylation of illite was found to be about 400°C in dry gas (Kristóf et al., 1985), therefore, it has a similar dehydroxylation temperature to kaolinite. Yau et al.

(1987) has treated illite hydrothermally over the temperature range from 360°C to 460°C at 300bars. They found that after 92 days, no significant changes happened to the illite samples. The experiments proved that illite is very stable under high water vapor pressure at about 400°C. Jeong et al. (2010) carried out TG analysis to pre-dried illite samples from room temperature to about 1000°C in air and found only 5% of weight was lost to the illite sample. Compare with the 25% weight loss when kaolinite is dehydroxylated, illite has little weight loss during dehydroxylation. One reason is because based on their structures, kaolinite has hydroxyl group concentration of 3.6 OH/nm^2, whereas for illite, it is 1.1 OH/nm^2 (Saada et al., 1995). According to the findings from literatures, dehydroxylation of

2.1.6 Other Clay Minerals

Besides kaolinite and illite, other common clay minerals are be chlorite (~1%), smectite (~0.3%), and mixed layer clays (~1.7%) such as kaolinite—smectite and illite—smectite (Masliyah et al., 2011). Even though the amounts of these clays are low compared to the kaolinite and illite, their special properties bring some issues to the oil sands processes. In smectite clays such as montmorillonite, the interlayer binding is weakened because isomorphic substitution occurs in the octahedron sheet and the compensating ions can be delocalized to the tetrahedron sheets. As a result, those compensating ions can be easily exchanged and water molecules can penetrate into the interlayers easily. Therefore, the CEC of smectite is very large compared to kaolinite and the volume of smectite can expend after it is wetted (Masliyah et al, 2011). Based on the research done by Kaminsky et al

(2009), more than 60% of the fines that have <0.2μm size fraction are mixed layer clays. This result suggests that in order to produce a solids-free bitumen, removal of the mixed layer clays could be an issue.

2.1.7 Non—Clay Fine Particles in Alberta Oil Sands

Even though clay particles play an important role in downstream bitumen processing, most minerals that Alberta oil sands contain belong to non—clay minerals. Kaminsky (2008) analyzed the mineral composition of different particle size fractions of Alberta oil sands. She commented that “over 90 mineral species had been identified in either Alberta oil sands or as their products of hydrothermal alteration, and many of these minerals are polymorphs, end members of a series of minerals, unofficial minerals, or just poorly characterized”. Their results showed that in bitumen froth, beside the common clay minerals mentioned in the previous section, more than 50% of the fine particles belong to non-clay particles. A detailed composition is tabulated in Table 2.1. The analysis was based on a single froth sample, mineral composition could vary depends on the ore deposition. It is worthwhile to analysis the mineral composition. From the table, even though the author showed that as the particle sizes decrease, clay minerals become dominant in composition(over 90% for the size fraction <2μm), bitumen froth prior to froth upgrading can still contain significant amount of large fines(2-45μm). Hence, it is worthwhile to consider the properties of these non-clays in the development of froth upgrading.

Table 2.1: Mineral Composition of Athabasca Primary Froth Based on XRD (Size fraction<45µm) (Kaminsky, 2008)

Minerals	Weight Percentage, %
Non-Clay Mineral	
Anatase	3.2
Brookite	2.1
Ilmenite	1.4
Lepidocrocite	0.5
Microcline	5.6
Pyrite	2.1
Quartz	29.3
Rutile	3.0
Schorl	2.1
Siderite	6.1
Zircon	2.1
Sub Total	57.5
Clay Mineral	
Kaolinite	18.7
Illite	11.3
Illite-Smectite	5.2
Kaolinite-Smectite	4.0
Chlorite	3.3
Sub Total	42.5
Total	100

2.1.8 Hydrothermal Reactions of Iron Minerals

According to previous section, there are significant amounts of pyrite (FeS_2) and siderite ($FeCO_3$) in the froth minerals. In oil sands, it is also very common to have dolomite ($CaMg(CO_3)_2$) and calcite ($CaCO_3$) (Helpler and Smith, 1994). Most carbonate exhibits oil-wet behavior based on some reservoir literature (Bennion and Thomas, 1992). Heavy, polar materials such as asphaltene strongly adsorbed on carbonate. Thus, it might be interesting to investigate the wettability alteration of carbonate in froth upgrading. These carbonates and sulfides provide inorganic sulfur and carbon to the reaction mixture. They might decompose if treated hydrothermally, and then the released carbon and sulfur could have an impact on the froth upgrading reactions. Carbonates decompose to form metal oxide and carbon dioxide. For example, siderite starts to decompose at 465°C in air based on thermogravimetric analysis (Alkac and Atalay, 2008). However, dolomite and calcite are unlikely to decompose if the temperature is under 500°C in air (Wieczorek-ciurowa et al., 1980). Once siderite decomposes, one of the products FeO, could react quickly with other species. The following reactions are proposed for only siderite in a hydrothermal system (Dhupe and Gokarn, 1989):

$FeCO_3 \longrightarrow FeO + CO_2$ (Eq 2.1)

$3FeO + CO_2 \longrightarrow Fe_3O_4 + CO$ (Eq 2.2)

$2Fe_3O_4 + CO_2 \longrightarrow 3Fe_2O_3 + CO$ (Eq 2.3)

$2FeO + CO_2 \longrightarrow Fe_2O_3 + CO$ (Eq 2.4)

$3FeO + H_2O \longrightarrow Fe_3O_4 + H_2$ (Eq 2.5)

$CO + H_2O \Leftrightarrow CO_2 + H_2$ (Eq 2.6)

At about 350°C, bitumen started to release hydrogen sulfide, H_2S. Unlike the rest liquid material in bitumen, it is much more mobilized that can penetrate into fine particles. According to Ko et al (2006), with the appearance of hydrogen sulfide, the following reaction can occur to the minerals at the temperature of 350-450°C. Fe_2O_3 and FeO can be provided by the product from Eq 2.1 Eq 2.3 and Eq 2.4, and hydrogen can be provided by radical H from hydrogen or by the product from Eq 2.5 and Eq 2.6. FeS, which is the product of Eq 2.7 and Eq 2.8, is called pyrrhotite. Pyrrhotite may not be exactly FeS. Sometimes it is nonstoichiometric and can be written as FeSx, with Fe to S ratio of (0.8-1):1. Fe, S ratio can be modified by the sulfur atom from hydrogen sulfide or sulfur atom from bitumen molecules (Details reaction equations are showed in Eq 2.12 and Eq 2.13)

$Fe_2O_3+H_2+2H_2S \rightarrow 2FeS+3H_2O$ (Eq 2.7)

$FeO+H_2S \rightarrow FeS+H_2$ (Eq 2.8)

Compared to carbonates, sulfides are more important since they contain unwanted sulfur. The most common sulfide in oil sands is pyrite, which is FeS_2. Because pyrite can be easily oxidized in air at elevated temperature, thermal decomposition of pyrite in nitrogen atmosphere has been investigated. FeS_2 decomposes into FeS and $S_{n.}$ It is found that if the temperature is below 500°C, the reaction rate is slow (Boyabat, 2004). Besides thermal decomposition of the pyrite, it may also react with water. The following reactions may occur if the temperature is over 440°C (Levy and White, 1988):

$3FeS_2+2H_2O \longrightarrow 3FeS+SO_2+2H_2S$ (Eq 2.9)

$SO_2+2H_2S \longrightarrow 3S+2H_2O$ (Eq 2.10)

Once the organics are involved in the reactions, it becomes even more complicated. According to Chadha et al(1997), the following reaction could occur:

$FeS_2 + (2 - x)H_2 \longrightarrow FeSx + (2 - x)H_2S$ (Eq 2.11)

$FeSx_1 + (x_2 - x_1)\ H2S \longrightarrow FeSx_2 + (x_2 - x_1)H_2$ (Eq 2.12)

$FeSx_1 + (x_2 - x_1)\,S \longrightarrow FeSx_2$ (Eq 2.13)

Eq 2.11 shows that pyrite can react with hydrogen generated from previously showed reactions or H radical cracked from bitumen. Eq 2.12 and 2.13 shows that sulfur atom from hydrogen sulfide or sulfur atom from bitumen molecules can enrich the sulfur in formed pyrrhotite.

Thus, it is necessary to use techniques like quantitative X-ray diffraction to test the stability of iron carbonate and sulfide after the hydrothermal reaction. The existence of iron carbonate and iron sulfide also can affect the element analysis results. To have accurate organic content adsorbed by the fines, inorganic carbon and sulfur content in the sample should be deducted from total amount.

2.1.9 Suggestions from Mineralogy Studies

Many mineralogical changes during hydrothermal reactions depend on reaction temperature and residence time. Those changes usually occur when the temperature is in the range of 400-500°C. The proposed froth upgrading temperature falls in this range. Consequently, it is important to carry out simulated froth upgrading reactions by just varying time and temperature. Although hydrothermal reactions of pure clay minerals have been studies, very few researches on oil-water-clay hydrothermal reactions have been done, especially analyzing the clay properties after the reaction.

2.2 Mineral-Organic Interactions

2.2.1 Mechanisms

Buckley and Liu (1998) did a review on mineral-crude oil interactions based on previous findings, and suggested the following list:

- Interactions between polar groups from oil and polar sites on minerals
- Asphaltene that is poorly dissolved in oil that can precipitate on mineral surface
- In presence of water, polar parts from oil and minerals can lose or gain protons to have acid/base interactions
- Ions such as Ca^{2+} can bind with mineral and oil components at the same time

Figure 2.5 shows a conceptualized image of how mineral particles are coated by organics from bitumen (Wang, 2013). Several articles have confirmed that clay minerals can never be totally covered by organics (Wang, 2013; Sparks et al., 2003), therefore, the partial coverage of the mineral surface is an important feature. Some researchers indicated that minerals are coated with both toluene insoluble and toluene soluble organics (Liu, 2002; Spark et al, 2003). However, a definition of organic components based on solubility does not apply to adsorption on a surface. For example, the adsorption of asphaltene on some clay minerals is found to be irreversible (Dean and James, 1986). Consequently, the use of the term "humic matter" by Sparks et al. (2003) as distinct from asphaltenes is not justified, since contacting kaolinite with apshaltenes is easily demonstrated to give irreversible adsorption. Instead, we will refer to this material that is not removed by toluene as “non-extractable organics”. The non-extractable organic materials coated on the fine solids have asphaltene like composition, based on elemental analysis (Kotlyar, 1998).

The mechanisms of asphaltene sorption on clay minerals are thought to be due mainly to interactions between the asphaltene surface groups such as carboxylic and carboxylate and the silanol and aluminol groups of the mineral (Jada and Debih, 2009). Some people have concluded that asphaltene adsorption on clay surface is Langmuir Isotherm (monolayer) (Dudášová et al., 2008). However, this argument is still debating. Jada and Debih (2009) stated that based on the polarity of solvent, the adsorption isotherm of asphaltene on clay surface can also be Type II(multilayers) based on chart provided by Brunauer et al (1938). Wang et al (2013) plotted the amount of asphaltene adsorbed by kaolinite as a function of asphaltene concentration. They found that the plot was suggesting Type I isotherm, but they stated based on previously observation of irreversible and multilayer adsorption, we must be cautious in treating the relationship.

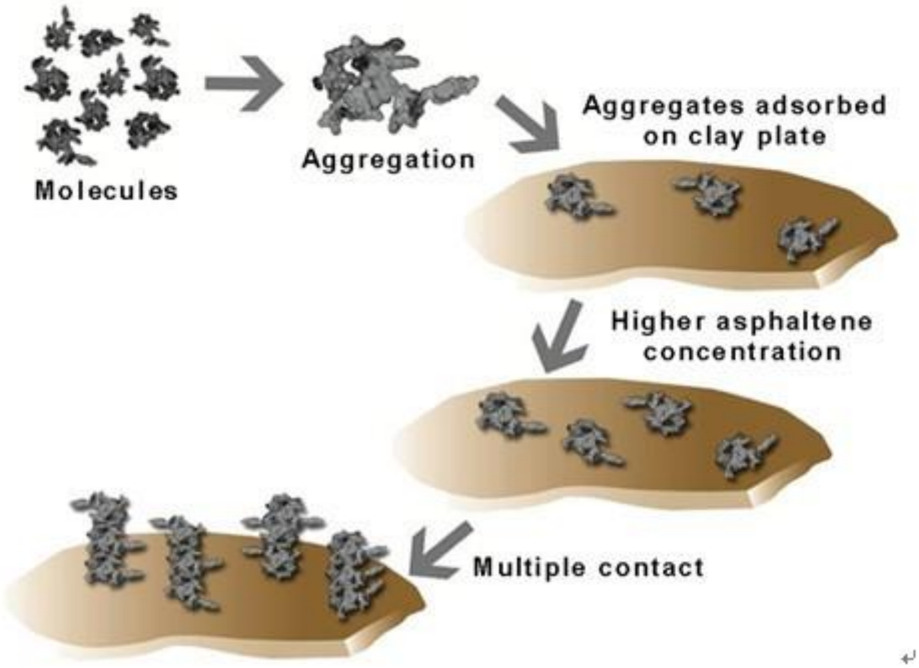


Figure 2.5 Conceptualized Image of Clay Minerals Coated with Organics in Oil Sands (Wang, 2013)

2.2.2 Factors Influencing Organic-Mineral Interactions

Mineral Types

The bitumen content in Alberta oil sands was found to be related inversely to the amount of clay minerals in the ore (Czarnecki, 1980). As stated in previous sections, fine solids are predominately clay minerals. Thus, fine clay minerals normally have larger surface area compare to those large sand grains. Ignasiak et al (1983) reported that minerals with decreased particles size and the amount of crystalline in the minerals tended to have more affinity to organic materials. As a result, clay minerals are significant in their surface and interfacial properties, and many process related issues such as stabilization of oil-water emulsions may be attributed mainly to the clay minerals. Among the common abundant clays in oil sands, kaolinite has the highest affinity to asphaltenes (Liendo, 2005). In oil reservoirs, kaolinite shows a preference to adsorb oil, while illite preferentially stays with brine. Based on X-ray absorption spectroscopies (XAS) and FTIR studies done by Bantignies et al (1997), hydroxyl groups on the alumina face and broken edges of kaolinite are most attractive to asphaltenes. They contacted asphaltenes with both kaolinite and illite, and stated that FTIR results showed the band at 3700 cm^{-1} (hydroxyl groups on the surface) were modified by the adsorbed asphaltenes. However, due to lack of surface OH groups, illite showed less interaction with asphaltenes. Based on XAS results, they confirmed the asphaltene adsorption process according to the order of Al atoms since only Al was linked to OH groups. However, in the paper, they only provided evidences that asphaltenes had interaction with surface OH group of minerals but they did not clarify why instead of water, asphaltenes were selectively interacted with OH groups. At last, they concluded that kaolinite tends to absorb more oil than water is because it has a higher hydroxyl group concentration as stated in the illite hydrothermal treatment section. Kaolinite is a very good mineral to use as modelling system based on three reasons provided above. First of all, it has high affinity to asphaltene compare to other minerals in oil sands. Secondly, bitumen froth contains large amount of kaolinite. Lastly, compare to the mixed-layer clays, kaolinite is easier to purchase and has higher homogeneity.

Aqueous Environment

Water can be easily adsorbed by minerals, and it is likely to form a thin layer in between mineral surface and the bitumen in oil sands. The asphaltene adsorption is reduced if the clay mineral is pre-wetted (Dean and McAtee, 1986). They also found that if kaolinite is pre-dried, the amount of asphaltene that can be coated on it is significantly increased because the adsorption of asphaltenes can be hindered by the adsorbed water. Based on this principle, injection of low salinity brine was used to enhance the oil recovery from the reservoir (Lager et al., 2006).

There are several hypothesizes to explain how different ions can change the interactions between mineral surface and organics. Lager et al. (2006) believe that multivalent cations on the surface of clay minerals can interact with polar organics such as asphaltene to form organo-metallic complexes. Such complexes will let more organics coat on the clay hence increase the hydrophobicity of clay minerals. Na^+, from brine can exchange with those multivalent cations to reduce the formation of the complexes, resulting more water-wet mineral surfaces. Another hypothesis similar to the previous one is that the penetration of saline water into the porous medium of clay minerals can take divalent cations such as Ca^{2+}, and hence increase the pH of the clay-organic interface. The generated OH^- can interact with acidic or basic material in the organic phase as well as the clay surface. These reactions will eventually release the organics from the clay surface (RezaeiDoust et al., 2011). Researchers also investigated salinity and pH effects on organic adsorption of specific clay types. For example, at low salinity and neutral pH, kaolinite has higher affinity for oil rather than water surroundings. However, with higher salt concentration, sorption of crude oil components is supressed because the sites are likely to be limited on the edges of kaolinite or both faces and edges are protected by the ions (Lebedeva and Andew, 2011). However, very few articles talked about the possible scenarios if clay and oil are both hydrothermally treated in the presence of varying water chemistry.

Temperature

The investigations of temperature effects on mineral-oil interaction are usually done at the conditions of petroleum reservoirs, therefore, normally those studies are with the presence of water. Bennion and Thomas (1992) found that the reservoir rocks became more hydrophilic once the temperature rose up to 265°C. They explained trend as due to the desorption of the polar components from the oil at elevated temperature. At high temperature, up to 250°C, oil-wet fines are mobilized so that they detached from the rock matrix. As a result, pores that those fines used to attach to become water-wet (Schembre and Kovscek, 2005). For some types of minerals, high temperature lowers the zeta potential of calcite, so that the repulsive force to the dissociated carboxylic groups increased. Thus, calcite becomes more water-wet (Hamouda and Gomari, 2006). If super critical water condition is considered, water starts to participate as catalyst and reactant (Siskin and Katritzky, 2001). Therefore, it can alter the local interaction between polar components of bitumen. However, no detailed studies have been done that how oil, water and mineral interact with each other at SCW condition.

2.2.3 Effects of Organic Coating on Fines

Wettability Alterations

The wettability of fines is an important property because it determines whether fines will be surrounded by water or oil, or prefers the interface between the two phases, which determines how easy those fines can be separated from an oil-water mixture. Dang-Vu et al. (2009) summarized the advantages and disadvantages of some wettability determination techniques. Most wettability measurements can only provide the apparent contact angle of fines with mixed wettability. The authors suggested that a sessile drop on a pressed disc can only provide rough ideas about wettability of the solids but it can measure wide range of contact angle values. In the case of this study, the main objective is to compare the wettability alteration of the fines after hydrothermal reactions, so sessile drop should be feasible. Compared to the bare clay minerals found in oil sands, bitumen components are much more hydrophobic. The advancing contact angle of water on a thin film of bitumen is above 90° (Vargha-Butler, 1988), whereas clay minerals without adsorbed bitumen components have an apparent contact angle below 30° (Wang et al 2013). Wang et al (2013) coated kaolinite with asphaltenes and found that the apparent contact angle of water on a pressed pellet of kaolinite increased from 17° to 88°. According to Figure 2.5, the resulting contact angle is likely intermediate between the clay mineral and bitumen because of the incomplete coating of the mineral surface.

Emulsion Stabilization

Mittal et al (2000) defined emulsions and foams as “complex fluid dispersions generally formed and stabilized by adsorbing surfactants, polymers, proteins, solid particles, or their mixtures onto fluid-fluid interfaces.” According to Mollet and Grubenmann (2001), bitumen froth matches perfectly the three basic conditions that required forming emulsions. Firstly, bitumen and water are immiscible and one can be dispersed in the other. Secondly, fine solids and asphaltenes act as emulsifying agents. Lastly, sufficient agitation can be provided by mixing in pumps and pipelines during the extraction process. In bitumen froth the emulsion is a water in oil emulsion. The concept of emulsion stabilization caused by fine solids is shown in Figure 2.6. Since many fine particles are partially coated with organic materials, those fines become biwettable. Part of one particular fine particle can be more oil-wet and part of it can be more water-wet. Those biwettable fines prefer to stay at oil-water interface in some certain orientation to keep their free energy the lowest. Hence steric barriers formed to prevent the coagulation of water droplets. Asphaltenes can also act similarly as a steric surfactant to stabilize emulsions. The emulsion stabilization caused by minerals is affected by many factors:

- Since particle size controls the ability of the particles to reside at the interface, this parameter may be one of the most important factors that affect emulsion stabilization (Tambe and Sharma, 1994). Schulman and Leja (1954) used barium sulfate particles to stabilize emulsions. They concluded that emulsions were stabilized if particle size was around 1μm, and if the particle size was more than 10μm, emulsion was poorly stabilized. The reason is because larger particles will only stabilize larger drops, which are less stable towards coalescence, and also gravitational forces on the particles become more significant. Tambe and Sharma (1994) also found that submicrometer to micrometer range sized fines can stabilize water in oil emulsions the best. Levine and Sanford (1985) tried to investigate water in oil emulsion stabilization from a thermodynamic point of view. They stated that most particles should be adsorbed in the water-oil interface by minimizing Helmholtz free energy associated with an oil-water interface stabilized by solid particles. They concluded that good particle size range to let this prevail was from 0.01μm-1μm.

- The concentration of fine particles is as important as the particle size distribution, since the emulsion stability may be proportional to the fines concentration. (Schulman and Leja, 1954; Tambe and Sharma, 1994; Levine and Sanford, 1985). Sztukowski and Yarranton (2005) found for the fine solids that have size range from 1μm to 10μm in Alberta oil sands, emulsions were stabilized only when the fines concentration was above 10kg/m^3. If the concentration was below that amount, those fines could even promote the coalescence of water droplets.
- Fines with contact angle of more than 90° are more likely to stabilize water-in-oil emulsions, while a contact angle of fines of less than 90° is more likely to stabilize oil-in-water emulsions; when the contact angle is close 90°, very stable emulsions will form (Tambe and Sharma, 1994; Bensebaa et al, 2000). However, if the particles are very hydrophilic (contact angle <20°) or very hydrophobic (contact angle > 160°), no emulsions will form. Yan et al (2001) tested the wettability of various minerals with different wettability. They concluded that those particles

with 90° contact angle did not always form the most stable emulsion. In fact, the nanosphere silica experiments they did showed that the most emulsion formed when the contact angle of the particles was 67°, which was double the amount of emulsion formed when the contact angle was 90°. This result suggests that it is necessary to test emulsion formation no matter what the contact angle of fines is. The contact angle of particles is also found almost proportional to the size of emulsion droplets (Yan and Masliyah, 1993). They used asphaltene coated kaolinite with D_{50}=0.2μm to form water in oil emulsions. When the contact angle is 26°, the emulsion droplets had size of 70 μm; when the contact angle is 40°, the emulsion droplets had size of 100μm; and when the contact angle is 140°, and the emulsion droplets had size of 240μm.

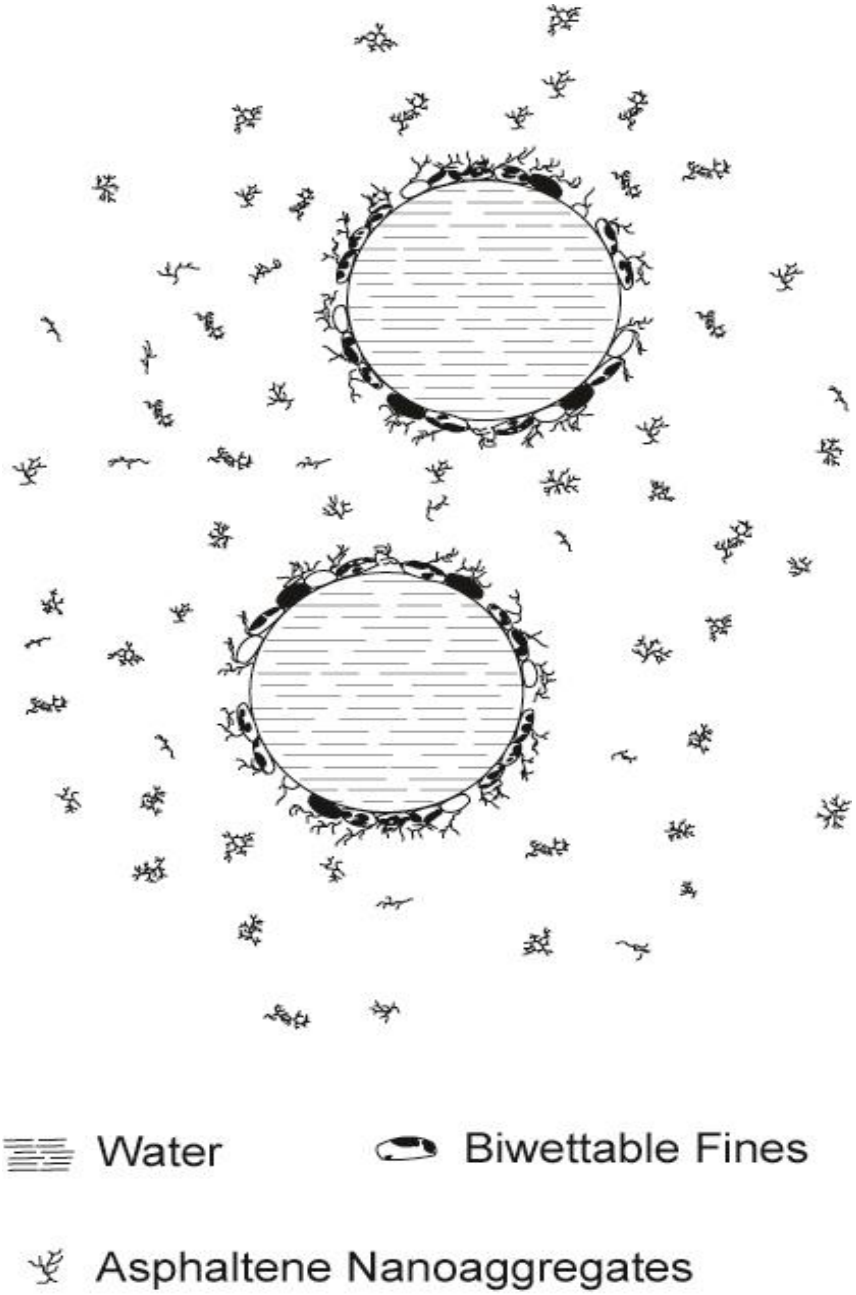


Figure 2.6 Clay Minerals Act as Steric Barrier to Prevent Water droplets from Coagulating (Modified from Sparks et al., 2003)

2.3 Related Industrial Process

2.3.1 Currently Employed Froth Treatment

Each oil sands mining company has their own process technology for froth treatment. The general approach is to add either naphtha or a paraffinic solvent to reduce the viscosity, to enable the removal of water and fine solids. Diluent, either naphtha or paraffinic solvent is added to bitumen froth to decrease the viscosity of the froth so that water droplets and fines can be centrifuged out. When paraffinic solvent such as hexane is added to the froth, about 7 wt% of the hydrocarbon will precipitate as asphaltene. The asphaltene will flocculate with fine solids and water droplets and the flocs can be easily removed (Dabros et al., 2004). However, the tailing produced by this technique contains asphaltene, which reduced the yield of revered bitumen. In both processes, the main environmental concern is the residual solvent that remains in the aqueous tailing stream. When naphtha is used as diluent, no asphaltene will precipitate but the produced bitumen contains more heavy organics compared to the bitumen after paraffinic treatments. Moreover, if naphtha is used, a significant amount of emulsified water droplets and fine solids cannot be removed from the produced bitumen. Typical concentrations of water and fine solids in this case are 3.5-5.0% and 0.5-0.8%, respectively (Masliyah and Gray, 2012). In contrast, paraffinic froth treatment produces dry, solids free bitumen at the expense of removing about 7% of the feed bitumen as flocculated asphaltenes. After removing the fines and water droplets, the diluted bitumen is sent to a diluent recovery unit (DRU). During this process, energy is needed to distill the diluent. Froth treatment contributes to the capital and operating costs of bitumen production, therefore, improvements to the froth treatments can be financially attractive and can be beneficial to the environment.

2.3.2 Bitumen Upgrading

Even though almost all the water and fines are separated after the froth treatment, “clean” bitumen still needs to be upgraded. By thermal cracking or hydrogenation, the viscosity of bitumen can be reduced so that it can be pipeline transported to downstream refineries, and its properties improved to command a higher price. Compared to light crude oil, bitumen normally has higher nitrogen, sulfur, and metal content. Thus, another purpose of bitumen upgrading is to reduce the undesirable content of these elements so that the product, which is “light sweet synthetic crude oil”, can be more commercially valuable.

A generalized bitumen upgrading process is shown in Figure 2.8 (Masliyah and Gray, 2012). “Clean bitumen” after naphtha-based froth treatment still contains about 0.8% of fines and some dissolved salts. At Syncrude, washing of the diluted bitumen after froth treatment is a further step to remove the salt and fine solids. Fresh water in the range of 7-10 vol% of the bitumen is added to wash the dissolved salts from bitumen. Then the water and some incremental fine solids can be centrifuged out. Sometimes, the water-in-oil emulsion is so severe that demulsifiers need to be added to break the emulsion.

After diluent is recovered from a diluent recovery unit (DRU), bitumen is sent to feed separation stage. Vacuum distillation is a widely employed technique in the feed separation stage. Some companies such as SUNCOR employ atmospheric distillation before a vacuum distillation. Atmospheric distillation is used for boiling point up to 343 °C, and under vacuum distillation, feed is further heated to 380-450 °C at 3-5kPa, light components (with boiling point up to 524°C) from the bitumen can be separated (Masliyah and Gray, 2012). The light components are normally sent to secondary upgrading for further cleaning, and the bottom product from vacuum distillation, which is called vacuum residue (VR), is sent to primary upgrading.

There are mainly two steps in primary upgrading which are coking and hydroconversion. Vacuum residue normally first undergo a hydroconversion process. This process uses temperature higher than 410 °C to give thermal breakage of chemical bonds. During the process, hydrogen is added to suppress coking, and because of the catalysts, hydrogenation of aromatics can occur. Normally, metal catalyst supported ebullated bed reactors are employed for hydroconversion process. Two similar licensed processes of hydroconversion are H-Oil and LC- Fining. The differences of these two are mainly equipment design (Masliyah and Gray, 2012). The product is then further cracked to form coke and light components in a coker. Coke is a carbonaceous solids that results from high temperature calcination of a carbon rich starting material (Masliyah and Gray, 2012). In oil sands industry, coke refers to toluene insoluble material due to severe cracking of bitumen. Coke has high carbon content as well as metal, solids, nitrogen and sulfur. Coking process is efficient for rejecting mineral solids and metals. Two coking processes are commonly employed: delayed coking and fluid coking. Delayed coking is a semi-batch process that feed is placed into large drums at about 500 °C. Light products are gradually removed and coke is accumulated in the drums until the drums are filled with coke. Delayed coking is widely used for large amount of feed and can produce green coke for commercial purposes. Fluid coking uses fluidized-bed reactor and is a continuous process. It normally operates at 510-500 °C and is suitable for small amount of feed because it requires shorter residence time compare to delayed coking (Masliyah and Gray, 2012). Coke formed in coking process is often sold for other industrial applications but sometimes oil companies gasify coke for energy.

Light components including the distillates from the separation process is then sent to secondary upgrading units mainly including hydrotreating and hydrocracking. Metal catalysts are used in hydrotreating units that allow the nitrogen, sulfur and metals to be separated. Light oil with low sulfur and nitrogen contents is then further cracked by bifunctional catalysts, which provide hydrogenation and acidic cracking. Finally, the light sweet synthetic crude along with by-products can be piped and shipped for further process (Masliyah and Gray, 2012)..

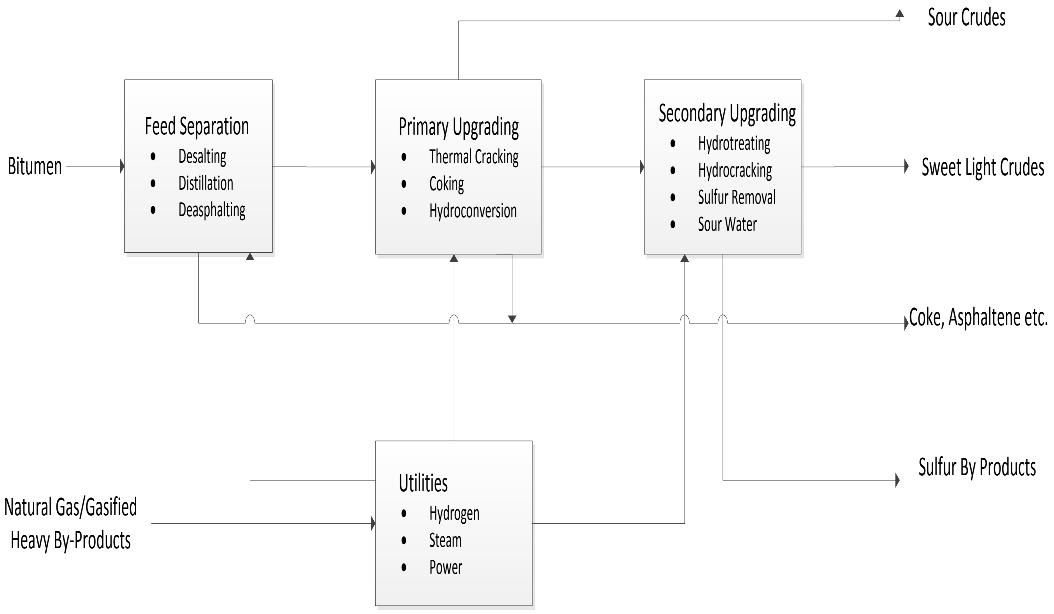


Figure 2.7 Scheme of Generalized Bitumen Upgrading Units (Masliyah and Gray, 2012)

2.4 Related Research in Froth Upgrading

2.4.1 Effect of Fine Solids on Upgrading

It has been reported that the appearance of fine particles in bitumen can inhibit the coke formation during the coking reactions (Tanabe and Gray, 1997). Coke fouling on the equipment is the main limitation of visbreaking, which can only achieve about 35% of conversion. With native fine solids, instead of fouling on process equipment, coke tends to form on the surface of the fines. Thus, visbreaking can achieve up to 60% conversion and the viscosity of bitumen dropped to pipeline transportable. Metal and sulfur removal is also enhanced by the higher conversion. The fines in thermal cracking process may have catalytic effect because organics contain with high sulfur content tends to adsorbed by the fine particles (Sankey et al., 1998). Hence there might be potential to decrease the cost of catalysts during upgrading processes.

Coking nucleation starts on the surface of fine minerals instead of process equipment. If fine particles are hydrothermally treated with bitumen at a relatively high temperature and long residence time, coke will form on the surface of the fines hence results a hydrophobic surface. This study should try to investigate the wettability change without coke formation. However, fines with coke can be a reference to compare the wettability alteration fines after the hydrothermal treatment.

2.4.2 Effects of Water on Upgrading

Water has been mixed with heavy hydrocarbon with API lower than 20° (e.g Alberta Bitumen and Venezuela heavy oil) to investigate its effect on cracking. Different temperatures and pressures have been applied as the reaction condition. Heavy oil cracked under super critical water conditions to form light hydrocarbons and heavy residues. At 410°C when the pressure is around 11MPa-13MPa, the amount of nickel and vanadium in the light hydrocarbons is at the minimum level(less than 20ppm). Surprisingly, the viscosity and specific gravity also reach the minimum at the same reaction condition (Murthy et al, 1984). This result is suggesting that in this study, similar reaction condition should first be tried.

Despite salts such as Cl^- is likely to react with water to form hydrochloride to corrode the equipment, the appearance of the salt significantly increase the oil quality after a hydrothermal reaction. Under supercritical water conditions, if heavy crude (11° API) is reacted with about 20wt% of brine water for about 30min, the product contains about 62 wt% light oil, which is much more than 2.4 wt% light oil in the case without adding brine. The API also significantly increased from 11° to 26°. Furthermore, if same hydrothermal reaction is compared to delayed coking, only 10 wt% of coke is formed instead of 30 wt%. Brine is effective when it is in the range of 2 wt%- 50wt% of the total reactants (Gregoli et al. 1989).

2.4.3 Upgrading of Bitumen Froth

As demonstrated in the previous sections, from just extracted bitumen to pipeline transportable crude oil, it requires a lot of processing. The proposed “froth upgrading” is to simplify bitumen processes to reduce the cost and environmental issues. During froth upgrading, bitumen with fines and water will first undergo a hydrothermal reaction, probably near super critical water condition with addition of additives to enhance some specific reactions. Then based on the characteristics of the major components such as fines, a separation procedure will be proposed to produce “clean” bitumen. Most papers and patents investigated the effect of water, effect of salt, and effect of fine solids individually. There is not much literature provides an overall outcome of directly upgrade the bitumen froth.

Even though studies are showing fines, salts and water in bitumen have positive effect in the reaction aspects of conversion, the mechanism of how those components in bitumen froth interact each other during reaction are poorly understood. In addition, the industrial issues such as corrosion in the equipment or the separation of these components still have not been solved. In this study, colloidal properties of fine particles need to be analyzed as well as to understand how their surface properties are modified by other components under reaction condition, hence to provide more systematic solutions to the industrial issues.

CHAPTER THREE
MATERIAL AND METHODS

3.1 Chemicals, Minerals and Sample Preparation

The reactants in the reactors consisted of four components: Fine particles, organics, water, and inert gas. Different reactions involved different components, which will be specified in the discussion section.

Toluene: Toluene (ACS Certified) was supplied by Fisher Scientific Co. and was used as diluent or washing solvent during the experiments.

Coated Kaolinite: Powder-like kaolinite sample was purchased from Ward's Natural Science, Ontario, Canada. The as-received kaolinite was treated with C7-asphaltene by immersing in an asphaltene in toluene solution (2 g/L) for 24 hrs. The coated kaolinite was then washed by toluene, and was vacuum filtered (0.22µm), then dried at 100°C for 24hrs.

Fines Extracted from Bitumen Froth: The sample of Athabasca bitumen froth was obtained from a pilot plant at Devon AB, courtesy of Imperial Oil. The froth sample was contained in a barrel. Because of long time of settlement, most water was on top of bitumen. To transfer bitumen froth out of the barrel, a large steel rod was used to stir the water, fines, and bitumen to be mixed thoroughly. Then the well-mixed bitumen froth was quickly scooped to a smaller container. Every time the froth sample was needed, thorough mixing was required. The well mixed froth sample contained approximately 8% of water and 7% of fines, according to Dean-Stark extraction measurement. To obtain the fine mineral particles, the bitumen froth was diluted with toluene at 1:1 ratio and centrifuged in a Beckman

Coulter centrifuge at 30000 RCF for 20 min. After the supernatant was siphoned out, the sediments were mixed with toluene and centrifuged again. The procedure was repeated 3-4 times until the supernatant was clear. The final sediments were dried and used as the fines from the bitumen froth.

Organics: To simulate the condition when upgrading bitumen froth, some organics were chosen to simulate the organics in the froth. 1-methylnaphthalene (1-MN) purchased from Aldrich-Sigma was chosen to simulate a most simplified condition of the reaction. Athabasca bitumen (Paraffinic Treated) was then used to simulate a condition with bitumen. The bitumen froth from which the fines were originally derived was used to provide the closest condition to froth upgrading.

Water: Deionized water filtrated by MilliPore was used as added water in most of the experimemts. Process water was used in a comparison experiment. The water chemistry of the process water was tabulated as in Table 3.1. The results were measured by using an iCAP 6000 Series ICP-OES Spectrometer.

Table 3.1 Water chemistry of Aurora Process Water

Ions	Al, mg/L	Ca, mg/L	Fe, mg/L	K, mg/L	Mg, mg/L	Na, mg/L	Si, mg/L	Cl, mg/L
Aurora PW	0.01	41.14	0.05	105.6	17.90	787.5	2.85	346.7

Inert Gas: Ultra-Pure Nitrogen purchased from Praxair was used as inert gas.

3.2 Hydrothermal Reactions in Micro reactors

3.2.1 Feeds and Reaction conditions

15mL stainless batch tube reactors (micro reactor) were used in the experiments. The reactor was made from tubes and fittings from Swagelok®. The apparatus is shown in Figure 3.1. The micro reactor was first tared then fines, organics, and water were loaded. Materials loaded in the micro reactors varied for comparison purpose. The different loads with their purposes are tabulated in Table 3.2. In most cases, 1g of fines and 1g of added organics were added for reaction. The amount of water added was based on simulation of final pressure at operating temperature using VMGsim, which will be discussed in next section. After the reactor was completely sealed, nitrogen which acted as inert gas was introduced to purge the air out from the reactor. After the first purge and fill up with 2.7MPa of nitrogen, the reactor was immersed in water to test leakage. If there was no leakage, air was further purged 5 more times and then the micro reactor was filled with nitrogen at 2.7MPa. Lastly, the micro reactor was completely immersed in hot sand bath heat to reaction temperature. The reaction time was normally 30min unless a time series was of interest. The reaction temperature was varied since the temperature effects needed to be analyzed. The temperature profile in the micro reactor is shown in Appendix C. The actual temperature in the sand bath after it reached equilibrium was slightly lower than the set-point temperature. It took about 2min for the reactor to reach the target temperature. After the reaction, the reactors were cooled under air blowing for 5min. The reacted kaolinite samples were washed first by 1-MN followed by pentane. The reacted fines were washed by toluene. Vacuum filtration was used in the washing process. The filtration apparatus was as shown in Figure 3.2. Filtrated fine was dried at 100°C for 24hrs. Each reaction was repeated at least once to ensure repeatability.

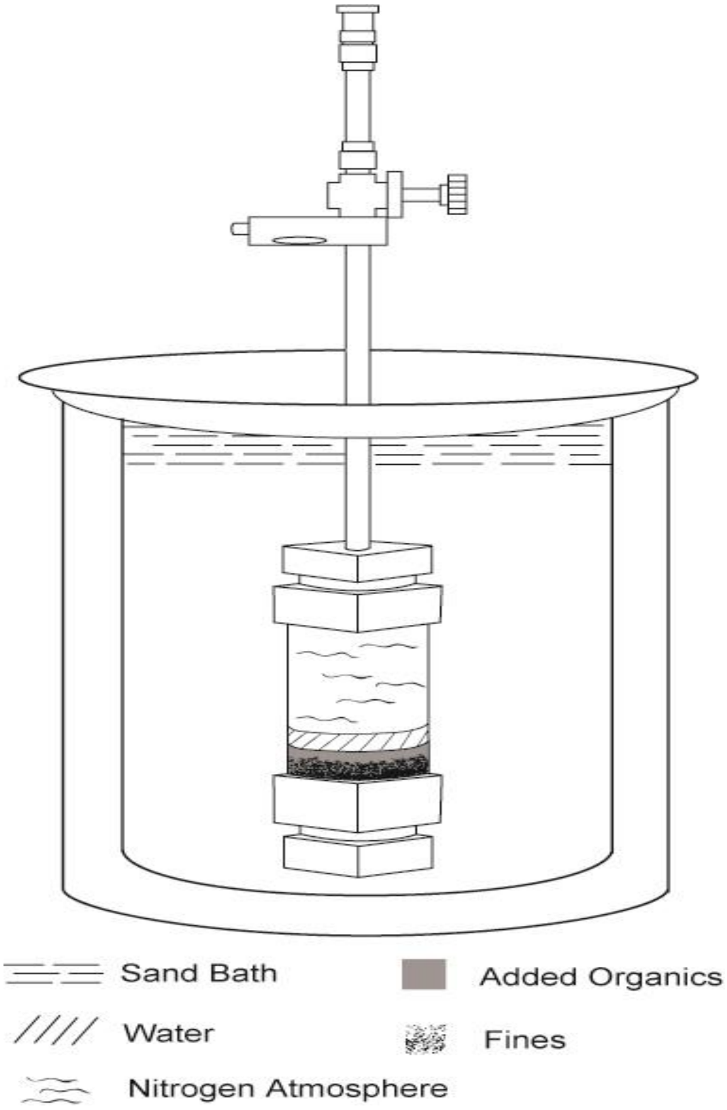


Figure 3.1 Schematic of batch tube micro reactor used in the study

Table 3.2 Summary of different reactions carried out in the study

Purpose	Loads			Reaction Specs.	
	Solids	Added Organics	Water	Residence Time	Temperature
Effect of Temperature	EF*	AB*	Pure Water	30min	352 °C
		BF*			362 °C
		DBF*			372 °C
					382 °C
	CK*	1-MN			392 °C
					402 °C
					432 °C
Effect of Time	EF	AB	Pure Water	15min	392°C
				30min	
				60min	
				120min	
Effect of Added Organics	EF	AB	Pure Water	30min	392°C
		BF			
		1-MN			
		DBF			
		N/A			
	CK	AB			
		1-MN			
		N/A			
Effect of Water	EF	AB	Pure Water	30min	392°C
			No Water		
	CK	1-MN	Process Water		

EF*: Extracted Fines; CK*: Coated Kaolnite; AB*: Athabasca Bitumen;

BF*: Bitumen Froth; DBF*: Direct Bitumen Froth is used (no solids added)

N/A: Not Added

3.2.2 Micro Reactor Phase Calculation

The maximum pressure allowed in the reactors at room temperature was 30MPa, based on the safe allowable stress on the reactor tubes. If the reactors were heated to 420°C, the pressure safety limit decreased to 20MPa. Hence the pressure in the reactor must be kept under 20MPa (normally was selected 15MPa as a safe condition). For safety purposes and to have more detailed information about the reaction conditions in the reactor, the conditions in the micro reactor were simulated by the software VMGSim. Sample simulation reports of 392°C reaction are included in Appendix A. Most of the pressure in the reactor was generated by water vapor and heated inert gas. Most of the reactions had temperature higher than the critical temperature of water, but the pressure was slightly lower than super critical pressure. Thus the reactions could be assumed to under hydrothermal condition, which is high temperature in the presence of superheated steam as a significant component of the vapor phase. Furthermore, since bitumen did not have fixed thermodynamic properties, the distillation curve of Athabasca bitumen according to Masliyah and Gray (2012), was input into VMGSim and then bitumen was cut into pseudo components with different boiling points. As a result, over the temperature range from 20°C-440°C, because of the high pressure that added water and inert gas generated, the amount of evaporated bitumen was negligible. In the simulation, only physical change was considered; bitumen cracking at high temperature was not included. As a result, at 392°C, the simulation showed that about 0.5 grams of water was enough to generate desired pressure of 15 MPa.

3.3 Analytical Techniques for Fine Solids

3.3.1 Contact Angle Measurements

Contact angle measurements were carried out to find the fine particles' static contact angle using a FTA200 Drop Shape Analyzer. About 100 mg of the fine particles were pressed into a pellet, 1 cm in diameter, by using an ICL 12TON E-Z PressTM pellet presser. The pressure was about 34MPa (5000 psi). One drop of deionized water was placed on the surface of the pellet, and microphotographs of the water drop were taken about one second after the drop completely contacted with the pellet. The contact angle was determined from the shape of the water drop. For each condition, 3-4 pellets were measured to ensure accuracy and repeatability.

3.3.2 Elemental Analysis

Elemental Analysis was carried out by using a VARIOMICRO Elemental Analyzer (Elemental Analysis, Hanau, Germany). About 10mg of different fines were combusted at 1200°C. The carbon, nitrogen, hydrogen and sulfur contents of the samples were measured. Every sample was measured at least three times so that error bars could be reported.

3.3.3 Scanning Electron Microscope (SEM)

Fines extracted from bitumen froth before and after the reaction were mounted on carbon shielded stubs and coated with carbon. The morphology of the fines was analyzed by a JEOL JAMP 9500F Scanning Electron Microscope (SEM). SEM images were obtained at an accelerating voltage of 10 keV with working distance 24mm, and magnifications of 5000X.

3.3.4 Energy Dispersive X-ray Spectroscopy Analysis (EDX)

Same mounted samples from SEM analysis were transferred to a Tescan Vega Energy Dispersive X-ray Spectroscopy. Important elements such as sulfur, aluminum, silicon, iron were semi-quantitatively measured. Different points on the fines were picked and measured to check the homogeneity of elements on different fine particles in the same sample. Results from EDX could be used as reference for comparison purposes.

3.3.5 Quantitative X-ray Diffraction Analysis (QXRD)

Quantitative X-ray Diffraction Analysis was carried out to measure the mineral composition of the fines. RockJock was used as a method to gain quantitative data. One gram of each sample that needed to be analyzed was added with 0.250 g corundum internal standard. The mixed samples were then grinded McCrone micronizing mill for 5 minutes with 4 mL ethanol. The ground samples were dried and shaken for 10 minutes in a plastic vial with 3 plastic balls and a small quantity of vertrel. Then the samples were sieved, sidepacked into a holder to ensure random sample orientation (Eberl, 2003). Rigaku Ultima IV diffractometer (40 kV, 44 mA) with Cu K-alpha radiation and a graphite monochromator was employed to generate X-ray from 5 to 65 degrees two-theta. XRD patterns gained from the analysis were then analyzed by JADE, which is a software that could provide a library of patterns of different minerals. Based on the peaks showing in the XRD pattern, all the minerals appeared in the sample were decided first. Then RkJock11 (Excel work book) was used to quantitatively determine the mineral compositions.

3.3.6 X-ray Photoelectron Spectroscopic Analysis (XPS)

Pellets for X-ray Photoelectron Spectroscopic Analysis were prepared followed the same procedure as in contact angle measurements. The analysis was performed using a Kratos Axis 165 spectrometer with monochromatic Al Kα radiation under vacuum condition. According to Wang et al (2013), XPS can only detect the elements up to 10nm from the surface. Therefore, XPS analysis can provide elemental analysis from the surface of the samples. Combine with other elemental measuring techniques, the differences of bulk and surface compositions changes due to the reaction could be investigated. Survey spectrums were performed to analyze all the elements possibly appeared, and high resolution spectrums were performed for more detailed information about carbon, sulfur, iron, aluminum and silicon. Calculations associated with XPS analysis in results section were based on survey spectra.

3.3.7 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS)

In order to verify and make some correlation to other elemental measurements, mass fractions of most elements in periodic table in the fines were quantitatively measured in Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). The analysis was conducted by using Perkin Elmer 's Elan 6000 ICP-MS(dual detector mode, 1300W). The results were reported in ppm, and the amount of each element was an average of three replicates.

3.3.8 Water-Oil Partitioning of Fines

The procedures for emulsion tests followed the methods of Yan (2001) and Dorobantu (2004). Emulsifying ability of fines was tested by mixing 0.2g of respective fines (unreacted fines and fines reacted with bitumen froth and water at 392°C) with 8mL water and 32mL of toluene in Teflon test tubes. Thus the solid concentration was 5kg/m^3, and the water volume fraction was 0.2. The test tubes were vortexed at maximum speed for 5min. Then the mixtures were transferred into two graduate cylinders. The cylinders were sealed and left for aging for 24 hrs. Then photos of the emulsion were taken and the volume of emulsions was compared to results from Yan's (2001) report.

For fractionating the fines, 1g of each unreacted and fines reacted with bitumen froth at 392°C was placed in Teflon separation funnels with 50mL water and 50mL toluene. Then thorough agitation was applied to the funnels. After that, toluene layer, aqueous layer, and rag layer were separated from the funnels. The separated layers were dried and then the fines they contained were analyzed.

3.3.9 Filtration Test

The filterability of the fines from bitumen froth is important to the industry. A lab scale filterability test was set up to test the filterability change of the fines due to the hydrothermal reaction. A schematic diagram the set up is shown in Figure 3.2. A vacuum pump was used to generate vacuum about -85kPa (pressure could vary during the filtration). Two grams of bitumen froth was directly hydrothermally reacted in a micro reactor at 392°C. Two identical batches (i.e 4 grams of bitumen froth) were partially diluted and transferred in a beaker. Four grams of each of the reacted and unreacted bitumen froth were diluted to 95mL with toluene. Four grams of Athabasca bitumen was also diluted into 95mL for reference purposes. Thus, there were three samples in total for filterability test. In order to filter the samples, the assembly was set up and the vacuum pump was turned on. Then the filter paper was rinsed by toluene. Once minimum pressure was reached, one 95mL sample was quickly stirred and poured in to the glass dam, and the fines that stuck with the beaker were rinsed off by 5mL of toluene. The total time required for that no visible toluene droplets remained in the glass dam was recorded as filtration time. The filtration time was compared for the three samples.

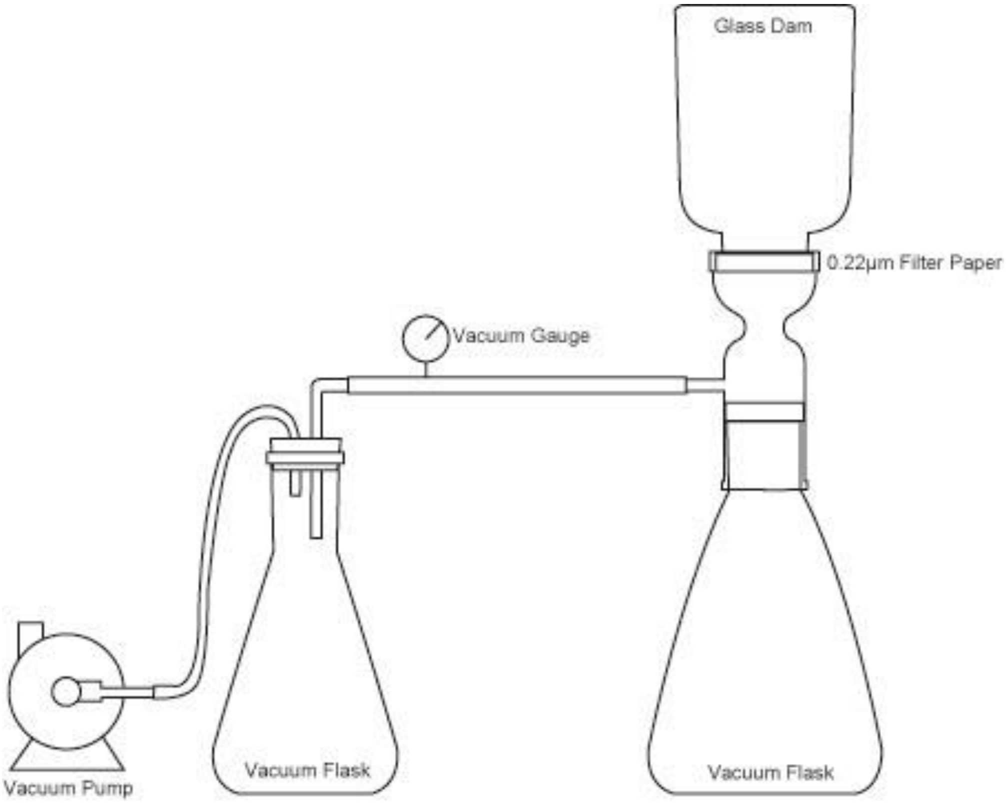


Figure 3.2 Schematic diagram of filtration test apparatus

3.3.10 Focused Beam Reflectance Measurement (FBRM)

A relatively new particle size measuring technology called focused beam reflectance measurement was employed to measure the particle size change of the fine particles. There are several advantages of this technology. First, it can measure the particles in any solution, not necessarily in water. Second, the liquid does not need to be transparent; the laser beam can go through dark coloured liquid. Third, it only requires very low concentration of particles, 0.1 % w/v is enough (Alex et al, 2002). Lastly, it can provide real time measurements if any changes occurred to the samples. A procedure was designed for FBRM measurements according to the advantages of FBRM. The fine particles tended to aggregate if they were dried. Ten grams of bitumen froth were weighed and five grams of it was dissolved in 300mL of toluene. The other half of the sample was divided into two identical halves and they were put into micro reactors with 0.2g of water at 402°C hydrothermal condition. Then the cooled reacted samples were directly dissolved in 300mL toluene. The two solutions were left undisturbed for 24hrs and then sonicated for 5min before the FBRM measurement. The solutions were transferred into 1L glass beaker to carry out the measurements. The impeller speed was set to be 400RPM to ensure no particles were still settled. In the solution, there were still significant amount of small water droplets, which came from the froth or the added water. Thus, the experiments were pulsed and the samples were heated at 175°C for half an hour. Then the heated samples were measured again to compare the particle chord length distribution with the not heated sample. The comparison of sample before and after heating was plotted in to a graph and included in Appendix D. The reacted and untreated fines' chord length distribution will be discussed in the result and discussion session.

CHAPTER FOUR
RESULTS

4.1 Mineralogy

Table 4.1 shows the mineral composition change of the fines due to the hydrothermal reaction. The results are gained based on Quantitative X- Ray Diffraction. The XRD patterns are included in Appendix B. The minerals are shown based on their weight percentage in the sample. Qualitatively, the mineral composition of extracted fines was very close to the solid sample from diluent recovery unit (DRU) feed analyzed by Liendo (2005). Illite and kaolinite were found to be the major clay particles in the sample. Chlorite was also found but it was hard to distinguish chlorite from the clay minerals because illite, kaolinite and chlorite shared some peaks in the XRD patterns. About 35wt% of the sample was contributed by non-clay minerals. The extracted fines contained very high iron content which resulted from about 20% of siderite and 5% of pyrite. Anatase and rutile, which contain titanium, were also found in the fines.

After the hydrothermal reaction, there were no mineralogical changes to the clay minerals. However, most of the siderite and pyrite reacted to become pyrrhotite, and some were oxidized to form magnetite. According to reaction Eq2.7-2.8 in the previous section, siderite likely reacted with hydrogen sulfide, which would be generated from bitumen if the temperature was over 350°C. Since hydrogen sulfide was mobilized and can penetrate into siderite, almost all the siderite can be converted. Sulfur atoms from pyrite could react with hydrogen (possibly with cracked hydrogen from bitumen) under the hydrothermal condition to form hydrogen sulfide. This partial hydrogenation would change the crystalline structure of pyrite to pyrrhotite. Because of the reaction of siderite, inorganic carbon was released, which may affect the total carbon content of the fines. Other than pyrite and siderite, the rest of the non-clay minerals were stable during the reaction.

Table 4.1: Mineral composition of the sample from quantitative XRD analysis

Mineral	Extracted Unreacted Fines, wt%	After Reaction with Bitumen at 392ºC for 30 min, wt%
Non-Clay Minerals		
Anatase	1	1
Magnetite	0	2
Quartz	5	4
Pyrite	6	0
Pyrrhotite	0	18
Rutile	3	3
Siderite	19	4
Subtotal	34	32
Clay Minerals		
Chlorite	8	12
Illite	17	16
Kaolinite	41	40
Subtotal	66	68
Total	100	100

4.2 Morphology

Figure 4.1 shows the SEM images of fines before and after the reaction. Both of the pictures show clear crystalline and layered structures of mineral particles. Organics could hardly be clearly identified in the image, therefore, the organic material was present as thin films. Based on SEM results, there were no significant changes to the morphology of the particles after the reaction.

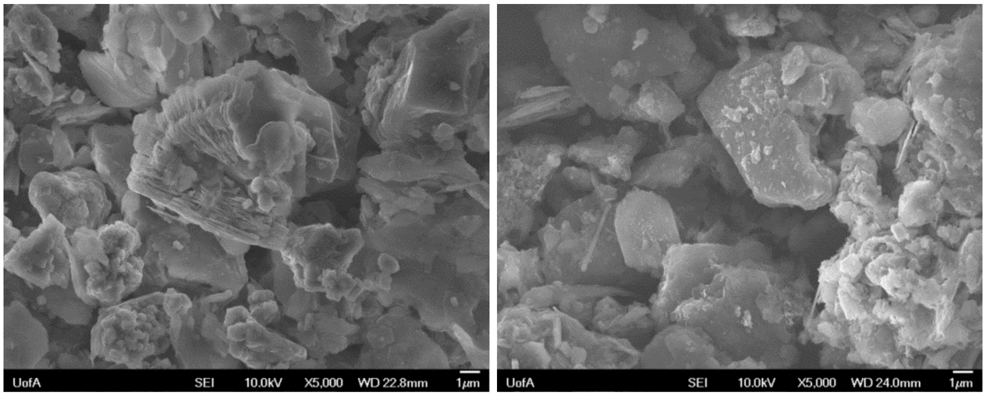


Figure 4.1: SEM images of fines: Left is before the reaction, right is reacted with bitumen froth at 392°C for 30min

4.3 Wettability

4.3.1 Contact Angle: Effect of temperature

Figure 2 shows the apparent contact angle of the fines under different reaction temperatures. From the chart, it can be observed that there was a significant amount of increase of apparent contact angles after the fines were hydrothermally reacted, which indicated a significant amount of hydrophobic organic materials precipitated or adsorbed on the fines' surface. The reaction temperature did have some effects on the final wettability of the fines. After the reaction at relatively low temperature (i.e 352°C in this case), the contact angle of the fines increased. The results suggested that the contact angle of the fines after reaction reached a maximum if the temperature was higher than a certain point (392°C was sufficient). Further increase in the reaction temperature did not give a further change in the contact angle value. Although there was some coke formed after the 432°C reaction, the contact angle did not give a significant increase. The contact angle of coke was tested to be more 100°. A reason that the contact angle of the fines never even got close to that of coke was likely because those minerals were not totally covered by organics (Wang et al, 2013).

In contradiction, the coated kaolinite model system showed a decreased trend of contact angle, which implied that the originally coated asphaltene on kaolinite had been washed away by 1-methylnaphthalene. Therefore, the results indicated that the kaolinite model system had very different mechanism during the reaction hence could not represent the reaction of authentic fines.

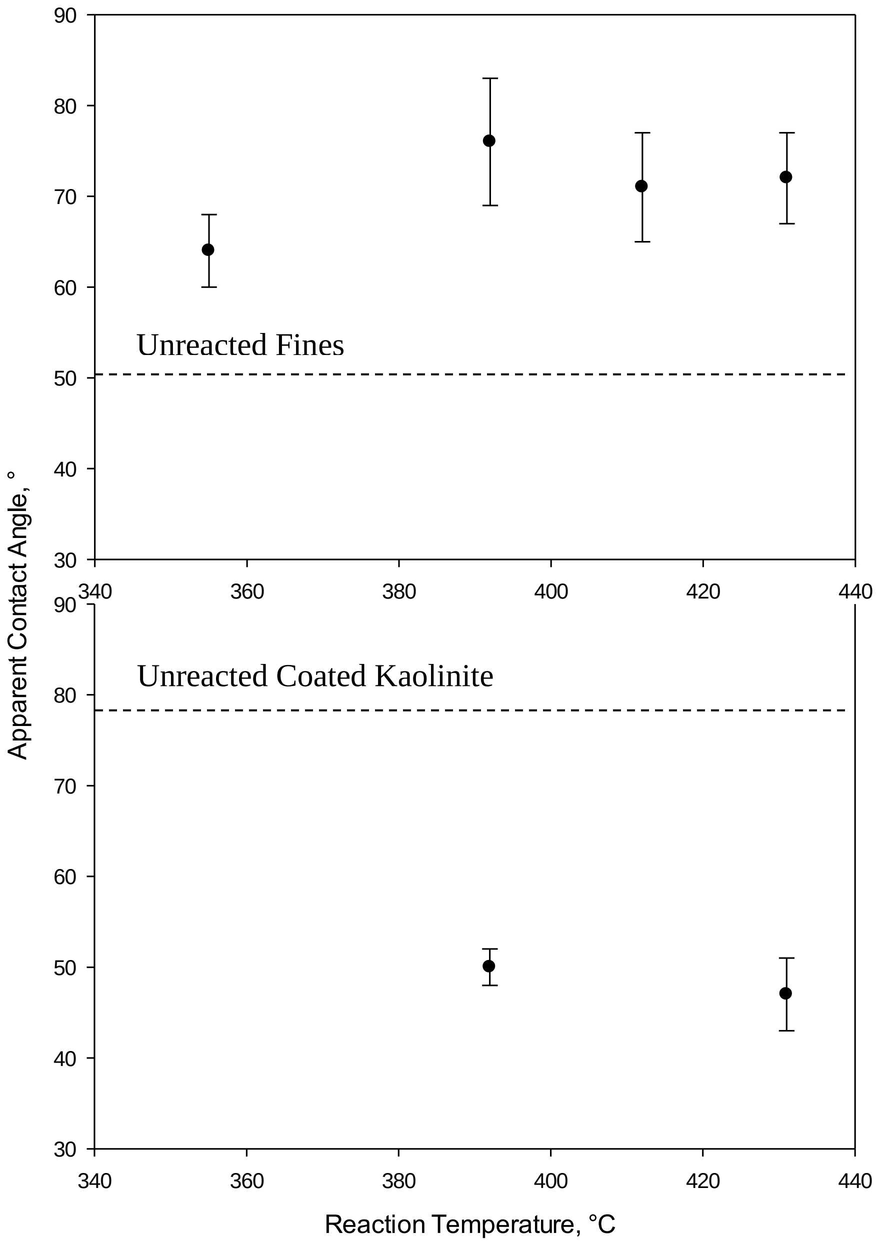


Figure 4.2: Apparent contact angle of the fines at different reaction temperatures. Top panel is authentic fines reacted with Athabasca bitumen and water. Bottom panel is coated kaolinite reacted with 1-MN and water. The contact angles of the samples prior to reaction are shown as horizontal lines for comparison.

4.3.2 Contact Angle: Effect of Time

Figure 4.3 shows the apparent contact angle of the fines after reactions at 392°C by varying residence time. As the temperature series, the contact angle of the fines increased after the reaction. Even after a short period of reaction, like 15min, the contact angle reached a value close to that observed after longer periods of reaction. This observation implied that the organic precipitation or adsorption on the surface of fines during the reaction was fast. The color of fines gradually became darker as the residence time was increased. However, the contact angle did not increase as the residence time increased. The contact angle after two hours reaction was almost the same as that of after 15min. One reason could be that the fines were never totally covered by organics, consistent with the results from the with the temperature series. Correlation with other techniques is needed to give more reasons for this observation.

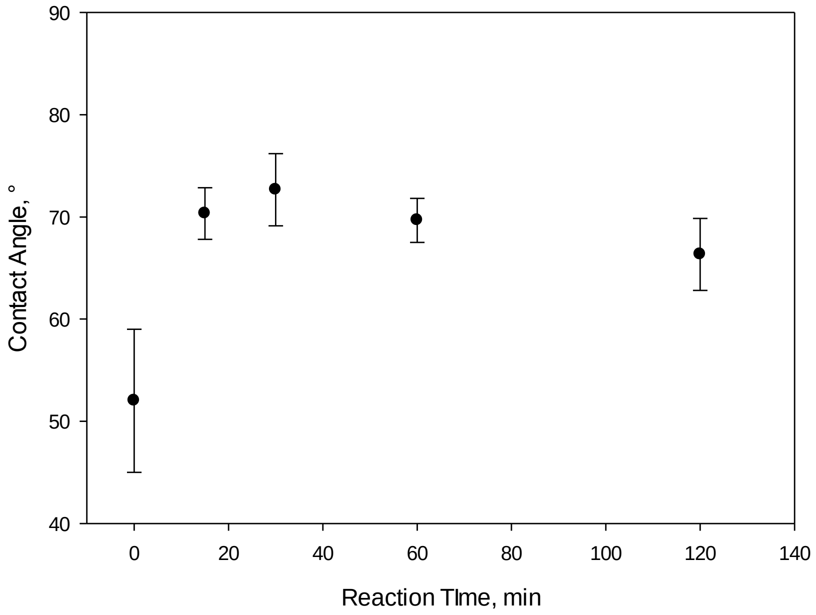


Figure 4.3: Apparent contact angle of the fines after reactions with different residence time.

4.3.3 Contact Angle: Effect of Added Organics

Different types of organics were reacted with minerals to provide comparisons with the bitumen contained in bitumen froth. All the combinations provided similar apparent contact angle results. Even without added organics, the contact angle increased to 66±2° compared to the unreacted fines. Along with the results gained from reacting with 1-methylnaphthalene, which was 66±9, the data indicated the organics originally coated on the surface of the fines, which could not be washed off during the extraction process, was sufficient to achieve a more hydrophobic surface of the fines after the reaction. Once bitumen was involved in the reaction, the measured contact angles did not increase significantly; 76±7 if bitumen was used and 78±7 if bitumen froth was used, within the error bounds of the contact angle measurements.

There might be some organics deposited on the surface of the particles from the added organics. This observation was clearer in the kaolinite model system: If bitumen was used as added organics, the measured contact angle was 72±2.0, which was significantly higher than when 1-methylnaphthalene was used. Based on the information provided by Table 4.2, it can be concluded that some organics originally associated with fines could be mobilized, and hence dissolve in the surrounding fluid phase and meanwhile, some organics also re-precipitated or attached onto the fines.

Table 4.2 Contact angle measurements of fines reacted with different added organics

Samples (392°C Reactions)	Contact Angle, °
Extracted Fine without added organics	66±2.0
Extracted Fine with 1-MN	66±9.0
Extracted Fine with Bitumen	71±7.0
Extracted Fine with Froth	78±7.0
Coated Kaolinite with 1-MN	50±2.0
Coated Kaolinite with Bitumen	72±2.0
Coated Kaolinite without Solvent	65±3.0

4.3.4 Contact Angle: Effect of Water

Table 4.3 shows the comparison of measured contact angles of fines reacted with water and process water added. To ensure there was as little water as possible, Athabasca bitumen with very little water dissolved in it was chosen as added organics. The pressure generated by water was compensated by adding extra nitrogen in the reactor. As a result, if water was absent during the reaction, the apparent contact angle was 88±4.0, which higher than contact angle of 71±7.0 when water was added. This result indicated that hydrothermal condition had some effect on changing the wettability of mineral surface. The kaolinite model system showed the same trend, that water helped asphaltene that originally coated on kaolinite's surface dissolve in 1-methylnaphthalene during the reaction. In addition, instead of deionized water, process water from Syncrude's extraction plant was used as added water. The apparent contact angle of process water reacted sample was 73±6.0, which indicated wettability of the fines after the reaction was not very sensitive to the cations dissolved in process water.

Table 4.3: Water effect to the contact angle measurements of fines after reaction

Samples (Reaction at 392ºC)	Contact Angle, °
Extracted Fines, with Bitumen and Water	71±7.0
Extracted Fines, with Bitumen without Water	88±4.0
Extracted Fines, with Bitumen and Process Water	73±6.0
Coated Kaolinite, with 1-MN and Water	50±2.0
Coated Kaolinite, with 1-MN without Water	62±2.0

4.4 Elemental Analysis

4.4.1 Carbon Content: Effect of Temperature

Even with some carbon in the form of inorganics in the mineral solids, carbon content analysis is still a very good way to test the total amount of organics retained by the fines. Figure 4.4 shows the carbon content analysis of the reacted samples under different temperatures. Reactions with different added organics are also included. After reaction at relatively low temperature such as 352°C, the fines lost significant amount of carbon content. From 352°C to 412°, carbon content of treated fines stayed in a close range but after reaction at 432°C, carbon content was higher than its original value. The increase of carbon content after high-temperature reaction was likely due to coke formation.

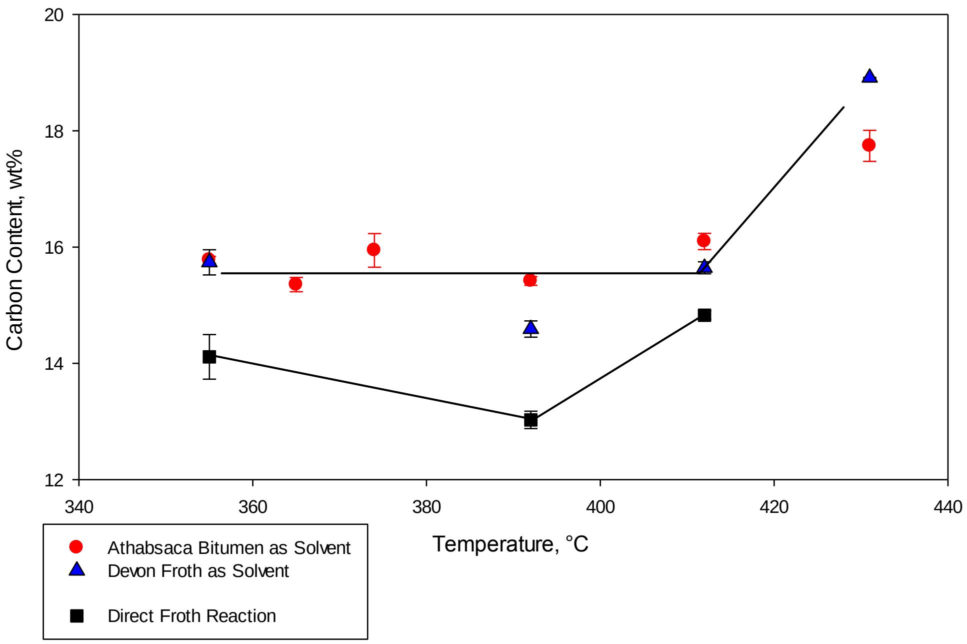


Figure 4.4: Carbon content analysis of the fines under different reaction temperatures. Direct froth reaction refers to the fines recovered reacted froth, with no prior separation and treatment.

4.4.2 Carbon Content: Effect of Residence Time

Figure 4.5 shows carbon content analysis of fines reacted with Athabasca bitumen with different residence times. The reaction temperature was 392°C. As shown in the graph, the carbon content decreased to a low level in a short period, which implied that dissolution of organics and reduction in carbon content was rapid. No significant change in carbon content was observed between 15min and 30min. However, carbon content started to increase if the residence time was long enough for coke formation. After two hours of reaction, the carbon content of the fines was even higher than the unreacted fines. The results agreed with the findings from the temperature series.

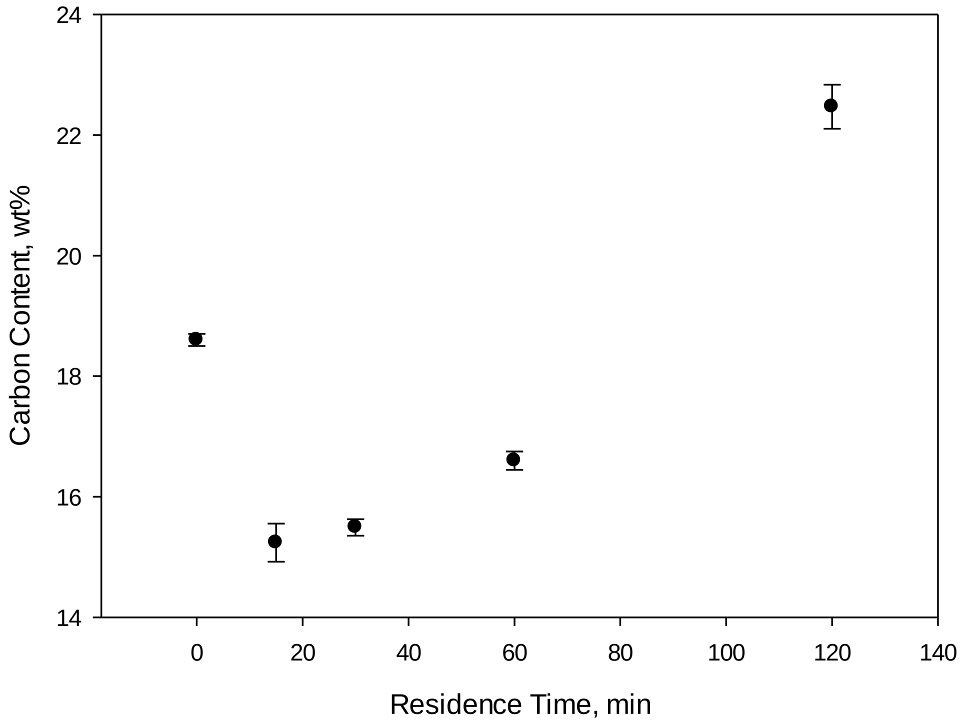


Figure 4.5 Carbon content analysis of the fines reacted in Athabasca bitumen with different residence times

4.4.3 Carbon Content: Effect of Added Organics

Table 4.4 shows carbon content analysis and XPS analysis of reactions with different added organics at 392°C. The samples without added organics tended to have higher carbon content, which implied that part of the organics originally from the fine particles dissolved in the surrounding fluid. If 1-methylnaphthalene was added, the carbon content after reaction was similar to the case with bitumen. If bitumen froth was directly reacted, the resulting fines had a lower carbon content. A possible reason is that in the actual froth, ratio of the fines to bitumen was much lower than the other two cases, and the fines in the froth were well dispersed, hence particles would have better contact with the fluid medium and would be less aggregated at the start of reaction.

The XPS results showed increased trends of carbon content if extra bitumen was added. indicating that bitumen components did precipitate or adsorb on the surface of the fines even though the total carbon contents were reduced.

The model system of coated kaolinite had much lower total bulk carbon content compare with authentic fines, which implied the authentic fines were not just simply coated with adsorbed asphaltene. Comparing the cases in the model system, the lowest carbon content was after reaction with 1-methylnaphthalene, and highest was after reaction with bitumen. If coated kaolinite was reacted with 1-MN, the organics originally coated on particles that had not been removed during preparation by washing by toluene were significantly dissolved in the 1-MN. If the coated kaolinite was reacted with bitumen, additional bitumen components deposited on the particles during the reaction. The authentic fines, on the other hand, were much more complicated, and the changes during the reaction could not be described only by those simple dissolution and adsorption depending on the liquid medium present. The high loading of organic carbon was resistant to significant changes under these conditions, except that the mineral surface was more uniformly coated when reactions occurred in the presence of a solvent, based on the XPS data.

Table 4.4 Carbon analysis and XPS analysis of reactions with different added organics at 392°C for 30min

Samples (392°C Reactions with Water)	Carbon Content, wt%	XPS, $\frac{C, wt\%}{Al+Si+Fe, wt\%}$
Extracted Fines without added organics	16.2±0.3	1.27
Extracted Fines with 1-MN	15.90±0.11	-
Extracted Fines with Bitumen	15.41±0.07	3.99
Fines from Direct Froth Reaction	13.02±0.15	3.53
Extracted Fines with Froth	14.59±0.14	3.64
Coated Kaolinite with 1-MN	1.92±0.16	0.69
Coated Kaolinite with Bitumen	3.74±0.27	0.90
Coated Kaolinite without Solvent	2.91±0.01	-

4.4.4 Carbon Content: Effect of Added Water

Carbon content after reaction of fines and bitumen with and without added water were found to be 15.41±0.07 wt% and 17.19±0.03 wt%, respectively. This observation agreed with contact angle measurements of the effect of water. The fines after reaction at hydrothermal conditions had lower bulk carbon content and were less oil wet than the fines from reaction without water.

<u>4.5 Particle Size</u>

4.5.1 FBRM Measurements

Figure 4.6 shows chord length distribution change (CLD) change after the bitumen froth was directly reacted at 402°C. Nighty percent of the particles had chord length smaller than 10μm. The mean chord length of unreacted fines was 5.69μm, and the median was 3.51μm. The mean chord length of 410°C direct reacted froth was 5.96μm, and the median was 4.19μm. In addition, the portion of very fine particles which were smaller than 1μm in chord length decrease from from about 0.4% to 0.2%. Particles larger than 10 μm were not affected by the reaction as much as the smaller particles. A separate measurement of unreacted fines was carried out on a different day, and it is also plotted in the same figure. The two pattern was almost identical, which indicates good repeatability. For the measurements on the second day, the mean chord length was 5.71μm, and the median was 3.54 μm. One more measurement of unreacted fines was carried out on third day. The pattern of the third measurement is not shown in Figure 4.6 for conciseness of the graph. For the three measurements, the mean chord length was 5.68 μm with standard deviation of 0.03 μm, and the median chord length was 3.53 with standard deviation of 0.02 μm.

Statistically, hydrothermal reaction increased particle size of the fines, especially for those fines with particle size smaller than 10 μm. However, the increase was small, and the results gained from FBRM were semi-quantitative. Furthermore, over the region of chord length more than 50 μm, unreacted samples have larger particle sizes. One reason could be that those hydrophic fines agglomerated in the toluene suspension. There is no single solvent that can disperse fines with different wettability well, hence measuring particle size of fines with heterogenious wettability can be difficult. A better measuring technique is necessary to better explore changes in particle size.

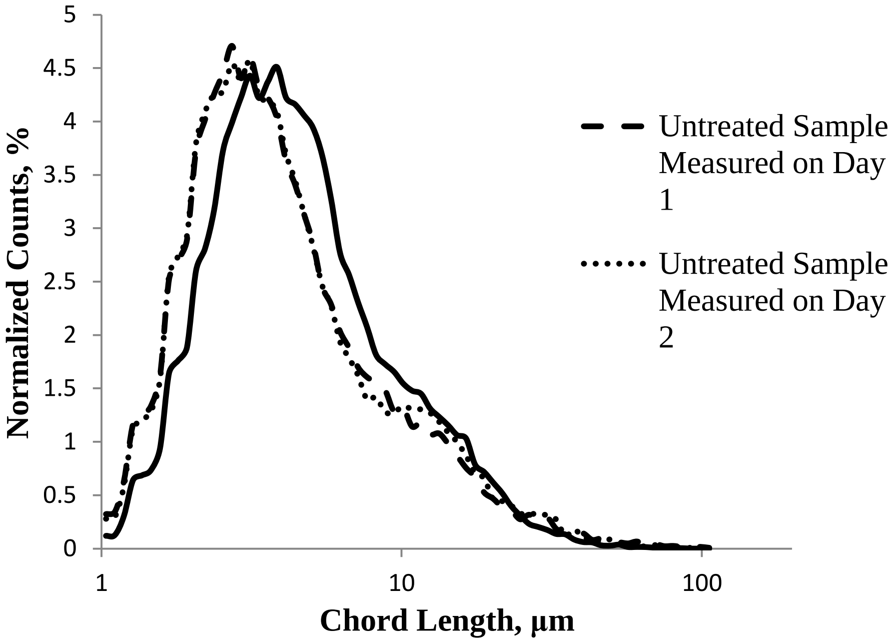


Figure 4.6 Chord length distribution change (CLD) for bitumen froth before and after direct reaction at 402°C

4.5.2 Filterability Test

Filterability of the fines significantly increased after the hydrothermal reaction. Based on filtration procedure decribed in section *3.4.9*, diluted bitumen froth plugged filtration paper very quickly, hence it could take an extremely large amount of time to finish. However, the filtration took about 240sec after the froth was directly reacted at 392°C and diluted. For comparsion, Athabasca bitumen (PFT) was diluted and filtered. It only took 40sec for the solution to pass though the filtration paper. The particle size increase described in previous section likley contributed to the significant increase of filterability.

4.6 Emulsion Tests

4.6.1 Water-Oil Partitioning of Fines

Figure 4.7 shows the emulsion volume measurements of untreated fines and the reacted fines. The mixture contained 20% volume fraction of water, which in this case was 8mL of water. After applying thorough shaking and 24 hours aging, toluene layer and water layer could be clearly identified, and there were rag layers formed in both cases. The rag layers tended to be in the aqueous layer of those two immiscible liquids. No emulsion could be observed in the toluene layer. This observation was in contradiction to the observation from Yan (2001) and Dorobantu (2004) that particles with contact angle of about 60° tended to form emulsions that were more than 40% in volume, and very few solids would stay in the oil phase. The volume of rag layer in the unreacted sample contributed roughly 70% of the aqueous layer (about 5% extra volume on a total volume basis). However, the volume of rag layer in reacted samples only contributed about 20% of the aqueous layer. For the fines after reaction, with contact angle in the range of 70-80°, they tended to stay in toluene phase; so after settling, a thicker layer of fines settlements could be observed. Some white-colored fines were observed on the bottom of the graduated cylinder for experiments which contains unreacted fines, but no solids were observed in the aqueous layer after the reaction. The fines fraction that stays in aqueous layer is normally the most hydrophilic fraction. The absence of these fines after reaction indicated that hydrothermal reaction conditions gave organic precipitation or adsorption on water-wet fines. Furthermore, the reacted fines settled much faster than the unreacted fines. After aging, most reacted fines settled on top of the aqueous layer and the toluene layer became clear, whereas the toluene layer stayed muddy since some unreacted fines had not settled. This observation implied that the effective particle size increased due the hydrothermal reaction, either due to cementation of the particles or due to more active aggregation in the suspension.

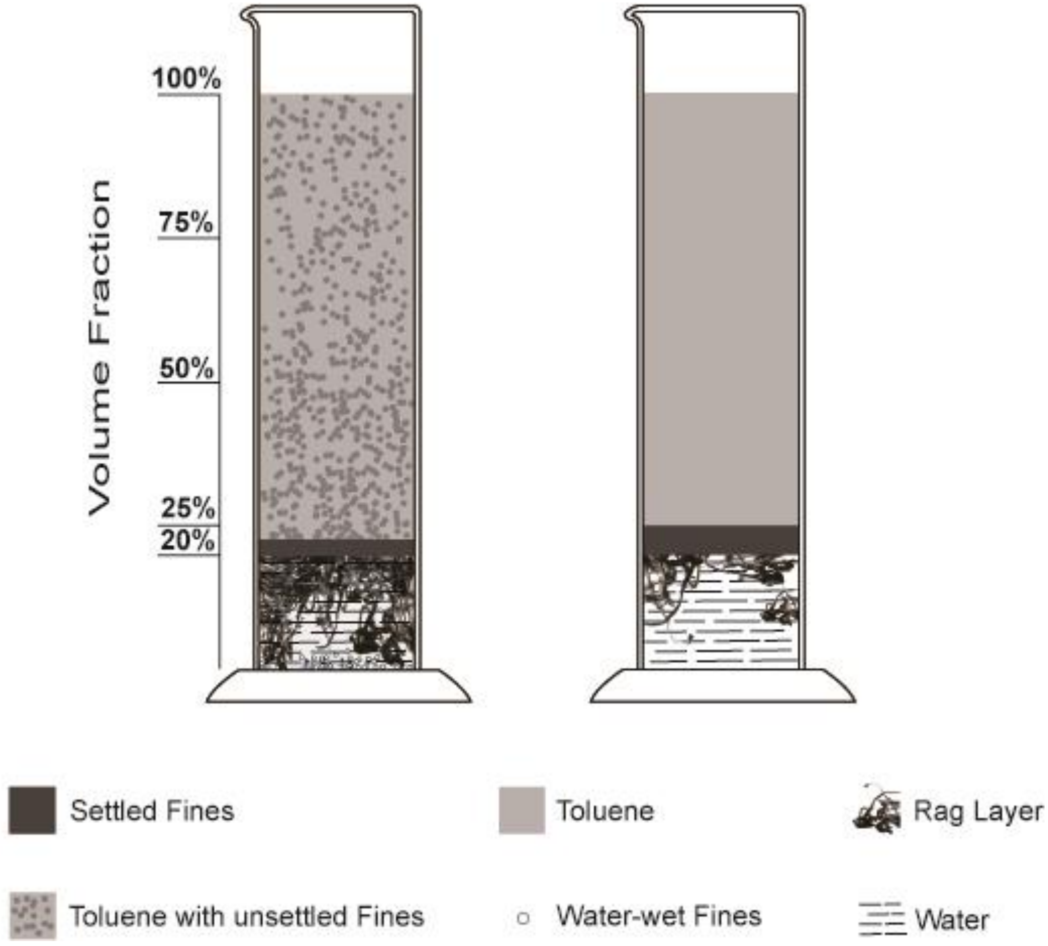


Figure 4.7 Emulsion volume measurements of unreacted fines (Left) and the reacted fines (Right)

4.6.2 Characterizations of Different Fines Fractions from Emulsions

Table 4.5 shows the amount of fines separated from each layer of the emulsion and as well as their carbon content. In the toluene layer of the unreacted sample, those well dispersed fines contained very high carbon content, but the amount of fines were small compare to the fines that stayed in the rag layer. The fines from the rag layer had lower carbon content. The total average carbon content of the fines was consistent with the weighted sum of these two fractions. Some very light colored fines could be separated from the aqueous layer, the carbon content of those fines were very low compared to the fines from other layers.

After the fines were reacted, most fines stayed in toluene layer but their carbon content was not as high as that of unreacted fines from toluene layer. The carbon content of the fines in the rag layer was lower than those fines from toluene layer, but the gap of carbon content was not as large as the unreacted fines. XRD (Appendix B) analysis was carried out on these fractions. The amount of these fines was limited so the XRD results were semi-quantitative. For the unreacted sample, based on the peaks, siderite and pyrite were slightly more concentrated in toluene layer than the rag layer. A high content of siderite can contribute to the carbon content in the fines from toluene layer. However, the carbon content of the fines in different layer was so different that siderite concentration was certainly not the only cause. The carbon content of fines in toluene layer significantly decreased after the reaction, and as described in the previous section, most fines stayed in toluene layer. There was still a difference in carbon content between the fines in toluene layer and the rag layer, but the gap was much smaller. The carbon content of the fines in different layers was significantly homogenized after the reaction.

Table 4.5 Weight fraction of fines separated from emulsion with carbon analysis

Samples	Weight % of Total sample	Carbon Content, wt%
Unreacted Total	-	18.6±0.1
Unreacted Toluene Layer	25.0	27.6±0.1
Unreacted Rag Layer	70.0	16.7±2.0
Unreacted Aqueous Layer	5.0	4.1±0.1
392°C reacted Total	-	15.4±0.3
392°C reacted Toluene Layer	75.0	16.8±0.4
392°C reacted Rag Layer	25.0	14.9±0.4

CHAPTER FIVE
DISCUSSION

5.1 Comparison of Different Measuring Techniques

5.1.1 Comparison of Carbon Compositions

Table 5.1 shows the carbon content measured by elemental analysis, XPS, and EDX of two samples. XPS and EDX are reported as carbon wt% divided by those wt% of the mineral structural cations, since these are semi quantitative measurements and in that way, it can provide better information on organic and mineral relationships. As previously stated, carbon content measured by elemental analysis showed an opposite trend compared to the contact angle analysis. For example, the extracted fines had a carbon content of 18.6±0.1 wt%. If the inorganic carbon. mainly provided by siderite is excluded, the remaining carbon content is very close to the AVR bitumen solids carbon content measured by Liendo (2005) which was 17%. After it was reacted with bitumen froth at 392°C, the carbon content dropped to 14.6±0.1 wt%, which meant less organics stayed with the fines after the treatment.

Results measured by EDX agreed, since the ratio of carbon to mineral structural cations decreased after the reactions. However, XPS showed results that agreed with the contact angle results. The carbon to mineral ratio significantly increased from 0.94 to 2.60 after the reaction. The signal of EDX can penetrate several micrometers into the sample whereas XPS can only go 7-10 nanometers deep down the surface of sample. Thus, one reason for the results can be that the total amount of organics decreased after the reaction, but organics tend to accumulate more uniformly on the surface of the particles. Signals of the mineral cations were significant in all cases, indicating that the minerals were only partly covered by organics. This result was consistent with Wang et al (2013). They stated even the surface was saturated with asphaltenes, XPS always showed signals of Al and Si, which indicated that kaolinite could never fully covered by asphaltenes.

The wt% of organics associated with unreacted fines was estimated to be 20% (Appendix C and Appendix F). From the Results section, we noticed that mineral changes during the reaction could cause the amount of inorganic carbon to decrease. Based on the QXRD results, 1.58% (Appendix C) of the carbon content was contributed by carbonate, as g carbon per 100 g of sample. If this amount of carbon content is deducted from the initial carbon content in unreacted fines, there is still about 17% of carbon content left, which is more than the measured carbon content after the reaction. Therefore, the carbon content decrease was not only caused by the decomposition of carbonate, but also the dissolution of organics originally coated on the fines. Based on these results, carbon content of the organics originally associated with fines was calculated to be 85.1% (Appendix C), which agreed with carbon content of Alberta bitumen and asphaltene reported (Wang et al, 2013; Czarnecka and Gillot, 1980; Dean and McAtee, 1986).

Table 5.1: Carbon content measured by elemental analysis, XPS, and EDX of two samples

Analyze Methods	Extracted Untreated Fine Particles	After 392°C, 30min Reaction with Bitumen Froth
Carbon Content, wt% (Elemental Analysis)	18.6±0.1	14.6±0.1
XPS, $\frac{C, wt\%}{Al+Si+Fe, wt\%}$	0.94	2.60
EDX, $\frac{C, wt\%}{Al+Si+Fe, wt\%}$	1.52±0.13	1.12±0.12

5.1.2 Comparison of Sulfur Compositions

Table 5.2 shows the sulfur content change due to the reactions via different analyzing techniques. Since the sample contained significant amount pyrite, the amount of inorganic sulfur needed to be excluded from the calculation. A sample calculation of the sulfur content is given in Appendix B. EDX and elemental analysis measured the bulk sulfur content of the samples, and the calculated results are close. Sulfur content in this case was reported as the ratio of sulfur to the abundant mineral structural cations. Different from the carbon analysis, sulfur content showed increased trends in all the measurements. Sulfur content increased about 17% after 392°C treatment based on elemental analysis, and 50% based on EDX. However, from XPS patterns, sulfur content increased almost 300% after the reaction. Sulfur content further increased if the fines were treated at432°C that was because coke formed.

Based on mineralogy results, the formation of pyrrhotite could contribute to the increase of sulfur content. In the following discussion, the results from 392 °C reaction with bitumen froth will be the main emphasis. Fines before the reaction contained 3.21% sulfur, 7.11% after the reaction (Appendix C). If the unreacted fines contain 80 % minerals and 20% organics as discussed above, sulfur content should increase by 3.12% after reaction due only to the mineralogical change. However, sulfur content only increased 0.57% after the reaction. This result again proved that a significant amount of organics that originally could not be washed off by toluene, dissolved into the organic phase during the reaction. In addition, the organics originally associated with fines contained 10% of sulfur (Appendix C) which was almost doubled the amount of sulfur in asphaltene reported in literature (Wang et al, 2013). However, sulfur content after reaction was mostly contributed by pyrrhotite, which implied that organic sulfur content associated with the fines before the reaction reacted to form pyrrhotite. The formation of pyrrhotite from siderite and pyrite could help to reduce the sulfur content by 0.21% if the fines content is 10% in the froth (calculation is attached in Appendix C) in the bitumen after the reaction. These results agreed with the results found by Sankey et al (1998) that minerals tended to adsorb sulfur leading to cleaner bitumen products.

Table 5.2: Sulfur content change by the reaction via different analyzing techniques

Analyze Methods	Extracted Fine Particles Untreated	After 392°C, 30min Reaction with Bitumen Froth	After 432°C, 30min Reaction with Bitumen Froth
Elemental Analysis, wt%	4.63±0.31	5.20±0.37	6.11±0.04
XPS, $\frac{S, wt\%}{Al+Si+Fe, wt\%}$	0.033	0.12	0.55
EDX, $\frac{S, wt\%}{Al+Si+Fe\ wt\%}$	0.088±0.01	0.12±0.03	0.16±0.02

5.1.3 Comparison of Other Elements

Table 5.3 shows the comparison of different mineral cations by using different measuring techniques. Among all the techniques, ICP-MS could provide the most accurate analysis. As stated in experimental section, EDX is only semi-quantitative. For QXRD, initially, same amount of each sample was loaded, but the actual weight of minerals were not the same. Empirical formulas were used for many minerals, and weight fractions of minerals were assumed to be 20% before reaction, 16% after reaction. Results from ICP-MS showed that almost all those elements increased by factor of 1.2 after the reaction. Results from EDX analysis agreed with ICP-MS quite well, normally within 1% of each element, giving exactly the same trend as shown from ICP-MS results. The amount of the elements calculated from QXRD results was higher than those from ICP-MS and EDX results, but an increasing trend was also observed. Since these elements would always be in the form of minerals, which could never be filtrated with organics or be generated during the reaction, the only explanation of this observation was that total the amount of elements other than the metal cation decreased. Loss of other elements could due to organic dissolution or mineral composition change.

Table 5.3 Comparison of the amount of structural cations in fines by using different measuring techniques

Elements	ICP-MS, wt%		EDX, wt%		QXRD, wt%	
	Unreacted	392°C with Froth	Unreacted	392°C with Froth	Unreacted	392°C with Froth
Aluminum	4.5	4.9	4.6	6.0	9.6	10.6
Silicon	-	-	7.2	8.1	13.0	13.1
Iron	8.0	9.6	8.6	9.3	11.6	15.5
Calcium	1.2	1.4	1.0	1.1	-	-
Magnesium	0.5	0.6	0.4	0.5	1.0	1.6
Titanium	1.2	1.4	1.6	2.0	1.9	1.9

5.2 Overall Effect of the Hydrothermal Reaction

A qualitative graphic summary of the overall effect to the fines after the hydrothermal reaction is shown in Figure 5.1. If bitumen froth is directly diluted, with toluene or other compatible solvents after applying sufficient agitation, an emulsion will be formed. Small water droplets are dispersed in diluted bitumen as shown on the left side in the figure. Many fines stay in the interface of water droplets and bitumen. Most of the fines at the interface are biwettable as discussed in literature section. Those fines and asphaltene aggregates act as steric barriers to prevent water droplets from coalescing, thereby stabilizing the emulsion. Fines can also be observed in the bitumen phase and within the water droplets. This situation indicates that the contact angle of unreacted fines was an average of sub-populations of fines with very different wettability. This proposition is further proved by the tests on fractionating the fines. The contact angle increased significantly after the reaction, and much less emulsion was stabilized. As shown on the right side of the figure, many emulsified water droplets coagulated after the reaction and formed an aqueous layer. Only a few fines remained at the water-bitumen interface, while most of the fines stayed in bitumen phase because of the precipitation or adsorption of organics on their surfaces. Water-wet fines can no longer be observed in the aqueous layer. The wettability of the fines is homogenized during the hydrothermal reaction. The carbon content of fines from different layers of emulsion, as discussed in *Section 4.6.2*, also becomes more uniform after the reaction. Furthermore, FBRM analysis indicated the increase of particle size. Thus, some fines are shown adhering together in the figure to represent agglomeration during or after the reaction.

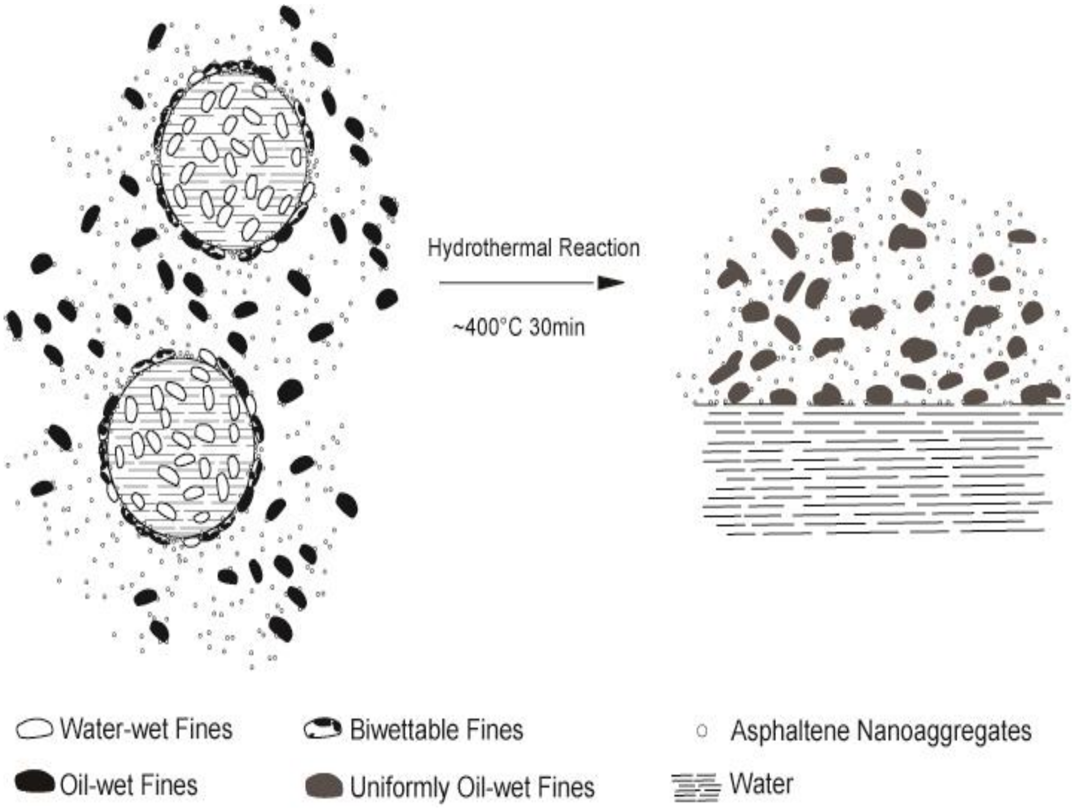


Figure 5.1 Graphical summary of the behavior of extracted fines before and after reaction in emulsion system

CHARPTER SIX
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Fine solids in typical bitumen froth samples were extracted by toluene and were hydrothermal reacted with water and different organics. The fines were characterized by different analyzing techniques and the following conclusions can be drawn:

1. Fine solids extracted from bitumen froth contained significant amount of organics (~20 wt. %). Those organics could not be visualized by SEM as distinct from the underlying mineral particles.
2. Mineral composition of the fines before and after reaction was measured by QXRD. About two thirds of the fines were clay minerals. The rest of the fines were contributed by non-clays. The sample contained significant amount of siderite and pyrite, which mostly converted to pyrrhotite after reaction. This reaction slightly reduced the sulfur content in bitumen. No other significant changes were observed in the mineral composition of the samples.
3. The apparent contact angle of unreacted fines was lower than that of reacted fines. However, the total carbon content of the fines decreased after reaction at 392°C for 30min. The changes of carbon content and contact angle were fast, completed within 15min. Longer residence time or higher reaction temperature could increase the carbon content(could due to coke formation) but the contact angle did not increase significantly.

4. The appearance of water in the reaction inhibited the contact angle and carbon content from increasing. The resulting contact angle and carbon content were not very sensitive to the water chemistry (pure water or process water).
5. After bitumen froth was hydrothermally reacted with water, then diluted by toluene, the filterability significantly increased. Based on FBRM test, the effective particle size of the fines increased after the reaction, which could contribute to the filterability increase.
6. Much less emulsion formed after the fines were reacted if the fines were mixed with water and toluene. Fines separated from different layers of the emulsion were found to have very heterogeneous color, carbon content, and mineral compositions before the reaction. However, after the fines were reacted, most of them would stay in toluene layer, and they had more uniform carbon content.
7. Use of coated kaolinite as a model system is not very helpful since the actual fines behaved very differently during the reaction.

6.2 Recommendations

For the extension of this study, the following recommendations are proposed:

1. A series of experiments should be carried out to understand how the appearance of water can inhibit the contact angle and carbon content from getting higher. This study would define an optimized water to froth ratio, to help reduce the cost of this type of treatment for industry application.
2. Establish a good method to compare particle size change after the reaction. We are facing several difficulties:
    a. Particle size is measured in toluene solution.
    b. Solution is very dark.
    c. Solution contains water droplets which can affect the results.
    d. Water-wet particles cannot disperse well in toluene and it is hard to find a single solution that can disperse all the fines with different wettability.
3. The froth sample investigated in this study contained high levels of much carbonate and sulfide, therefore, froth sample from other sources should be analyzed the same way.
4. Since a high carbon content was found associated with fines that could not be washed by toluene, a method needs to be developed to observe how the organics and minerals are combined. SEM failed the task; therefore the method selected must be able to observe structure at a length scale below one micron.

REFERENCES

Alkac, D., and Atalay, U. (2008), "Kinetics of thermal decomposition of Hekimhan–Deveci siderite ore samples." *International Journal of Mineral Processing* 87.3-4, 120-28.

Bantignies. J. L., Moulin. C.C.D., Dexpert. H. (1997), “Wettability contrasts in kaolinite and illite clays: characterization by infrared and X-ray absorption spectroscopies,” .*Clays Clay Miner.* 45, 184–193.

Bensebaa, F., Kotlyar L. S., Sparks, B. D., and Chung, K. H. (2000), "Organic coated solids in Athabasca Bitumen: characterization and process implications." *The Canadian Journal of Chemical Engineering* 78.4, 610-16.

Bennion, D.B. and Thomas, F.B. (1992), “Formation damage due to mineral alteration and wettabilitychanges during hot water and steam injection in clay-bearing sandstone. “, *1992 SPE Symposium on Formation Damage Control* (Feb 26-27, 1992, Lafayette Louisiana.).

Boyabat, N. (2004), “Thermal decomposition of pyrite in the nitrogen atmosphere." *Fuel Processing Technology* 85.2-3, 179-88.

Brunauer, S., Emmett, P.H. and Teller, E. (1938), “Adsorption of gases in multimolecular layers”. *J. Am. Chem. Soc*., 60, 309--319.

Buckley, J. S., and Liu, Y. (1998), “Some mechanisms of crude oil/brine/solid interactions.” *Journal of Petroleum Science and Engineering*, 20, 155–160

Chadha, A., Stinespring, C. D., Stiller, A. H., Zondlo, J. W., and Dadyburjor, D. B., (1997), "Characterization and activity of ferric-sulfide-based catalyst in model reactions of direct coal liquefaction: effect of preparation conditions." *Industrial & Engineering Chemistry Research* 36.2, 284-95.

Chen, F., Finch, J.A., Xu, Z., and Czarnecki, J. (1999), "Wettability of fine solids extracted from bitumen froth." *Journal of Adhesion Science and Technology* 13.10, 1209-224.

Czarnecka, E., and Gillot, J. E. (1980), “Formation and characterization of clay complexes with bitumen from athabasca oil sand." *Clays and Clay Minerals* 28.3, 197-203.

Dabros, T., X. Yang, Y. long and H. Hamza (2004), “Settling properties of paraffinic solvent-diluted bitumen emulsions”, *5th International Conference on Petroleum Phase Behavior and Fouling*., Banff, Alberta.

Dang-Vu, T., Jha, R., Wu, S., Tannant, D. D., Masliyah, J., and Xu, Z. (2009), “Wettability determination of solids isolated from oil sands." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 337.1-3, 80-90.

Dean, K. R, and McAtee, J.L. (1986), “Asphaltene adsorption on clay." *Applied Clay Science* 1.4, 313-19.

Dhupe, A., and Gokarn, A. (1990), "Studies in the thermal decomposition of natural siderites in the presence of air." *International Journal of Mineral Processing* 28.3-4, 209-20.

Dorobantu, Loredana Stefania (2004), *Stabilization of Oil/Water Emulsion by Hydrophobic Bacteria*., M.Sc Thesis. University of Alberta, Alberta

Dudášová, D., Simon, S., Hemmingsen, P. V., and Sjöblom. J., (2008): "Study of asphaltenes adsorption onto different minerals and clays Part 1. experimental adsorption with UV depletion detection." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 317.1-3 1-9

Eberl, D. D. (2003), “User’s guide to RockJock—a program for determining quantitative mineralogy from powder X‐ray diffraction data”., *US Geological Survey*, Open‐File Report No. 03‐78.

Gregoli, A.A., Oko, U.M., and Leder, F., (1989), “Process for converting heavy crudes, tars and bitumens to lighter products in the presence of brine at supercritical conditions”, in USPTO 4818370

Grim, Ralph E. *Clay Mineralogy*; McGraw Hill Book Company Inc.: New York, 1953.

Guggenheim, S. (1995), "Definition of clay and clay mineral: joint report of the AIPEA nomenclature and CMS nomenclature committees." *Clays and Clay Minerals* 43.2, 255-56.

Hamouda, A.A. and Gomari, K.A.R. (2006), "Influence of temperature on wettability alteration of carbonate reservoirs." , *2006 SPE/DOE Symposium on Improved Oil Recovery* (April 22-26, 2006, Tulsa, Oklahoma.).

Heath, A. R., Fawell, P. D., Bahri, P. A. and Swift, J. D. (2002), "Estimating average particle size by focused beam reflectance measurement (FBRM)". *Part. Part. Syst. Charact.*, 19, 84–95.

Helper, L.G., and Smith, R. G. (1994), *The Alberta oil sands: Industrial procedures for extraction and some recent fundamental research*. AOSTRA technical publication series no. 14. Edmonton: Alberta Oil Sands Technology and Research Authority.

Hurst, V J., and Kunkle, A. C. (1985), "Dehydroxylation, rehydroxylation, and stability of kaolinite." *Clays and Clay Minerals* 33.1, 1-14.

Ignasiak, T., Kotlyar, L., Longstaffe, F., Strausz, O., and Montgomery, D. (1983), "Separation and characterization of clay from Athabasca asphaltene." *Fuel* 62.3, 353-62.

Jada, A., and Debih, H. (2009), “Hydrophobation of clay particles by asphaltenes adsorption." *Composite Interfaces* 16.2, 219-35.

Jeong, E et al. (2010), "Effects of physicochemical treatments of illite on the thermo-mechanical properties and thermal stability of illite/epoxy composites." *Journal of Industrial and Engineering Chemistry*

Kaminsky, Heather Anne Welling. (2008), *Characterization of an Athabasca oil sands ore and process streams.*, Ph. D Thesis. University of Alberta, Alberta

Kaminsky, H. A. W., Etsell, T. H., Ivey, D. G., and Omotoso, O. (2009), "Distribution of clay minerals in the process streams produced by the extraction of bitumen from Athabasca oil sands." *The Canadian Journal of Chemical Engineering* 87.1, 85-93.

Kasperski, K. L. (2001), “Review of research on aqueous extraction of bitumen from mined oil sands”. [Division No. CWRC 01-17 (CF)]. Natural Resources Canada, CANMET-WRC.

Kristóf, J., et al. (1985), "Study of the dehydroxylation of clay minerals using continuous selective water detector." *Thermochimica Acta* 93, 625-628

Ko, T., Chu, H. and Tseng, J. (2006), "Feasibility study on high-temperature sorption of hydrogen sulfide by natural soils." *Chemosphere* 64.6, 881-91.

Konan, K. L., Peyratout, C., Bonnet, J., Smith, A., Jacquet, A., Magnoux, P. and Ayrault, P. (2007), "Surface properties of kaolin and illite suspensions in concentrated calcium hydroxide medium." *Journal of Colloid and Interface Science* 307.1, 101-08

Kotlyar, L.S., Sparks, B.D., Woods, J. R., Raymond, S., Le Page, Y. and Shelfantook, W. (1998), “Distribution and types of solids associated with bitumen." *Petroleum Science and Technology* 16.1-2, 1-19.

Lager, A., Webb. K. J., Black. C. J. J., Singleton. M., Sorbie. K. S. (2008), “Low salinity oil recovery – an experimental investigation” *Petrophysics*, 49, 28–35

Lebedeva, E. V., and Andew, F. (2011), "Wettability alteration of kaolinite exposed to crude oil in salt solutions." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 377, 1-3 115-22.

Levine, S., Sanford, E. (1985), “Stabilisation of emulsion droplets by fine powders”, *The Canadian Journal of Chemical Engineering* 258–268

Levy, J., and White, T. (1988), “The reaction of pyrite with water vapour." *Fuel* 67.10, 1336-339.

Liendo, Janeth. (2005), *Fundamental Study of the Roles of Fines in Upgrading*. M.Sc. Thesis. University of Alberta, Alberta

Masliyah, J H., Xu, Z., and Czarnecki, J. A. (2011), *Handbook on Theory and Practice of Bitumen Recovery from Athabasca Oil Sands*. Cochrane, Alta.: Kingsley Knowledge Pub., 177-203.

Masliyah, J., and Gray, M.R. (2012), *Extraction and Upgrading of Oil Sand Bitumen Intensive Short Course*. Calgary, Alberta.

Mittal, K. L., and Promod K. (2000), “Foam and emulsion stability: interfacial rheology and thin liquid film phenomena” *Emulsions, Foams, and Thin Films*. New York: Marcel Dekker, 131

Mollet, H., and Grubenmann, A., Eds. (2001), Formulation Technology-Emulsions, Suspensions, Solid forms, WILEY-VCH, Federal Republic of Germany.

Murthy, A.K.S., Kundanbhai, M.P., and Bekker, A.Y. (1984), 'Process for production of light hydrocarbons by treatment of heavy hydrocarbons with water', in USPTO 4446012

Omotoso, O. (2004), "High Surface Areas Caused by Smectitic Interstratification of Kaolinite and Illite in Athabasca Oil Sands." *Applied Clay Science* 25.1-2, 37-47.

RezaeiDoust. A., Puntervold. T., and Austad. T. (2011), “Chemical verification of the EOR mechanism by using low saline/smart water in sandstone.” *Energy & Fuels*, 25.

Saada, A., B. Siffert, and E. Papirer. (1995), "Comparison of the hydrophilicity/hydrophobicity of illites and kaolinites." *Journal of Colloid and Interface Science* 174.1, 185-90.

Sankey, B.M., Maa, P.S., and Bearden, R. Jr. (1998), 'Conversion of the organic component from tar sands into lower boiling components', in USPTO 5795464

Shang, J., M. Flury, J. B. Harsh, and R. L. Zollars. "Comparison of Different Methods to Measure Contact Angles of Soil Colloids." *Journal of Colloid and Interface Science* 328.2 (2008): 299-307

Schulman J.H., Leja J. (1954), "Control of contact angles at the oil-water-solid interfaces: Emulsions stabilized by solid particles (BaSO4)" *Trans. Faraday Soc.*, 50, 598

Siskin, M. and Katritzky, A. R. (2001), "Reactivity of organic compounds in superheated water: General background", *Chemical Reviews*, 101 825-35.

Sparks, B.D. et al. (2003), "Athabasca oil sands: effect of organic coated solids on bitumen recovery and quality." *Journal of Petroleum Science and Engineering* 39.3-4, 417-30.

Sōmiya, A., Hishinuma, K., and Akiba, K. (1995), "A new materials processing—hydrothermal processing." *Bulletin of Materials Science* 18.6, 811-18.

Sreekumar, A. (2013) “2 Major threats to Canada's oil Sands producers” http://www.fool.com/investing/general/2013/04/30/2-major-threats-to-canadas-oil-sands-producers.aspx

Sztukowski, D., and Yarranton, H., (2005), "Oilfield solids and water-in-oil emulsion stability." *Journal of Colloid and Interface Science* 285.2, 821-33.

Tanabe, K. and. Gray, M. (1997), "Role of fine solids in the coking of vacuum residues." *Energy & Fuels* 11.5, 1040-043.

Vargha-Butler, E. I., Potoczny, Z. M., Zubovits, T. K., Budziak, C. J., and Neumann. A. W. (1988), “Surface tension of bitumen from contact angle measurements on films of bitumen." *Energy & Fuels* 2.5, 653-56.

Wang, S. et al. (2013), “Study of asphaltene adsorption on kaolinite by X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectroscopy” *Energy & Fuels* 27 (5), 2465–2473

Wang, Shanshan. (2013), *Characterization of asphaltene composition and asphaltene adsorption on kaolinite* . Ph. D. Thesis. China University of Petroleum, Beijing

Wieczorek-ciurowa, K., Paulik, J. and Paulik, F. (1980), "Influence of foreign materials upon the thermal decomposition of dolomite, calcite and magnesite Part I. Influence of sodium chloride." *Thermochimica Acta* 38.2, 157-64.

Yan, N. et al. (2001), “On water-in-oil emulsions stabilized by fine solids” *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 193, 97–107

Yan, Y., and Masliyah. J. H. (1993), “Solids-stabilized oil-in-water emulsions: scavenging of emulsion droplets by fresh oil addition." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 75, 123-32.

Yau, Y. et al. (1987),"Hydrothermal treatment of smectite, illite, and basalt to 460°C: Comparison of natural with hydrothermally formed clay minerals." *Clays and Clay Minerals* 35.4, 241-50.

Yeskis D. et al. (1985), “The dehydroxylation of kaolinite" *American Mineralogist*, 70, 159-l64

Appendix A. Sample VMGSim Simulation of the Reaction Condition

Assumptions: Fines only occupy a small volume of the reactor with no contribution to the pressure change. One gram of fines only occupied less than 0.5 mL volume. VMGSim can only simulate continuous flow processes. Hence to simulate a batch reactor, the calculation needs to be done to cancel out the time unit on the flow rate. For example, in the 392°C simulation, the mass flow was 1960 kg/hr, and the volume flow was 14.5 m^3/hr, so 14.5 m^3 of volume was occupied by 1960 kg of reactants. In our case, 1.96g total reactants were in 14.5mL batch tube reactor.

Table A.1 Sample VMGsim simulation of fines reacted with bitumen and water in 15mL micro reactor at 392°C.

Name	**Bitumen**	**Pure_Nitrogen_Simulation**	**Reactor_Condition400°C**	**Water_&_Nitrogen**
Description				
Upstream Op			**Batch_Tube_Reactor.Out**	
Downstream Op	**Batch_Tube_Reactor.In1**			**Batch_Tube_Reactor.In0**
VapFrac	0.00	1.00	0.93793	1.00
T [C]	**400.0**	**25.0**	392.6	**400.0**
P [kPa]	**16000.00**	**2757.9028**	16000.00	**16000.00**
MoleFlow/Composition	Fraction kgmole/h	Fraction kgmole/h	Fraction kgmole/h	Fraction kgmole/h
Mass Flow [kg/h]	**1000.00**	471.30	1950.00	**950.00**
Volume Flow [m3/hr]	1.019	**15.000**	14.516	13.949
Std Liq Volume Flow [m3/hr]	0.918	1.479	2.831	1.913
Std Gas Volume Flow [SCMD]	1.4476E+3	9.5656E+3	2.6361E+4	2.4913E+4
Energy [W]	1.716E+5	3.961E+4	4.115E+5	2.399E+5
H [kJ/kmol]	242606.6	8475.1	31950.1	19710.1
S [kJ/kmol-K]	649.270	138.995	196.346	169.724
MW	392.77	28.01	42.06	21.68
Mass Density [kg/m3]	981.7079	31.4198	134.3313	68.1040
Cp [kJ/kmol-K]	1024.723	30.527	99.550	45.043
Thermal Conductivity [W/m-K]	0.1379	0.0261	0.1116	0.0873
Viscosity [Pa-s]	1.8271E-7	1.7817E-5	2.4454E-5	3.0085E-5
Molar Volume [m3/kmol]	0.400	0.892	0.313	0.318
Z Factor	1.2510	0.9904	0.9275	0.9252
Surface Tension				
Speed of Sound				

Appendix B XRD Results of Fines and Emulsion Fractions

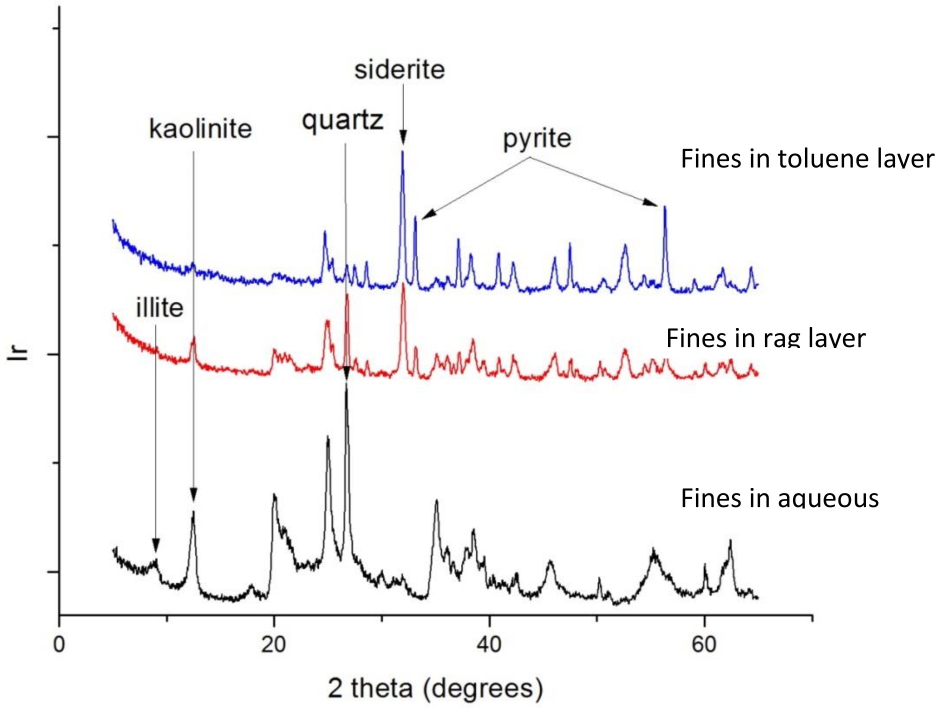


Figure B.1 XRD patterns of different fractions separated from toluene-water emulsion

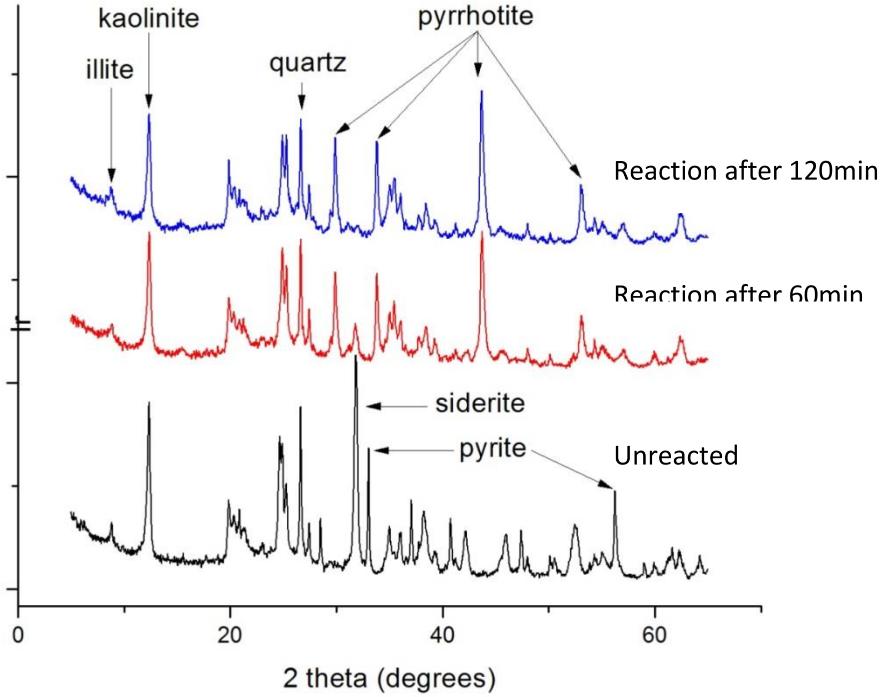
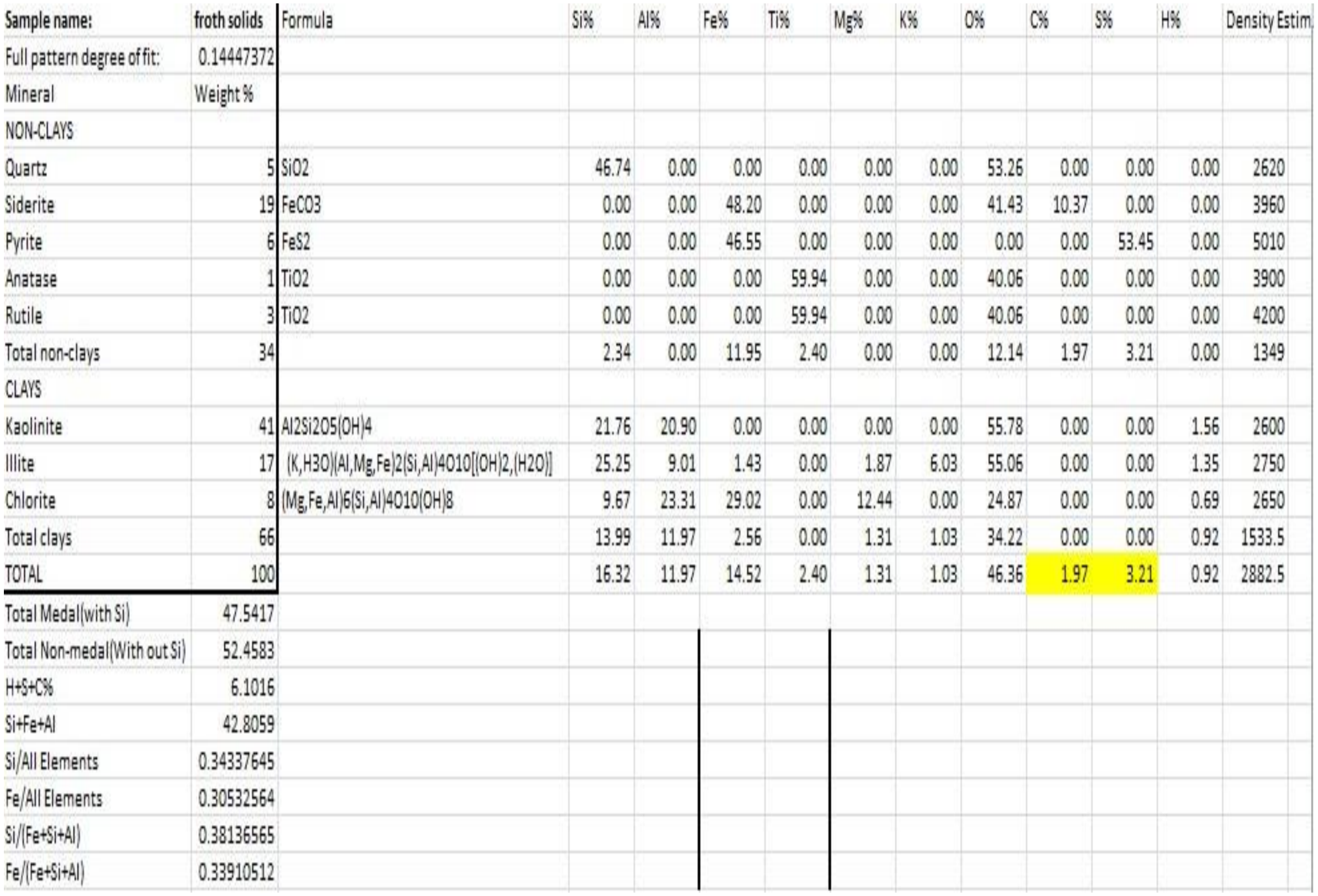


Figure B.2 XRD patterns of fines reacted with Athabasca bitumen for varied residence time

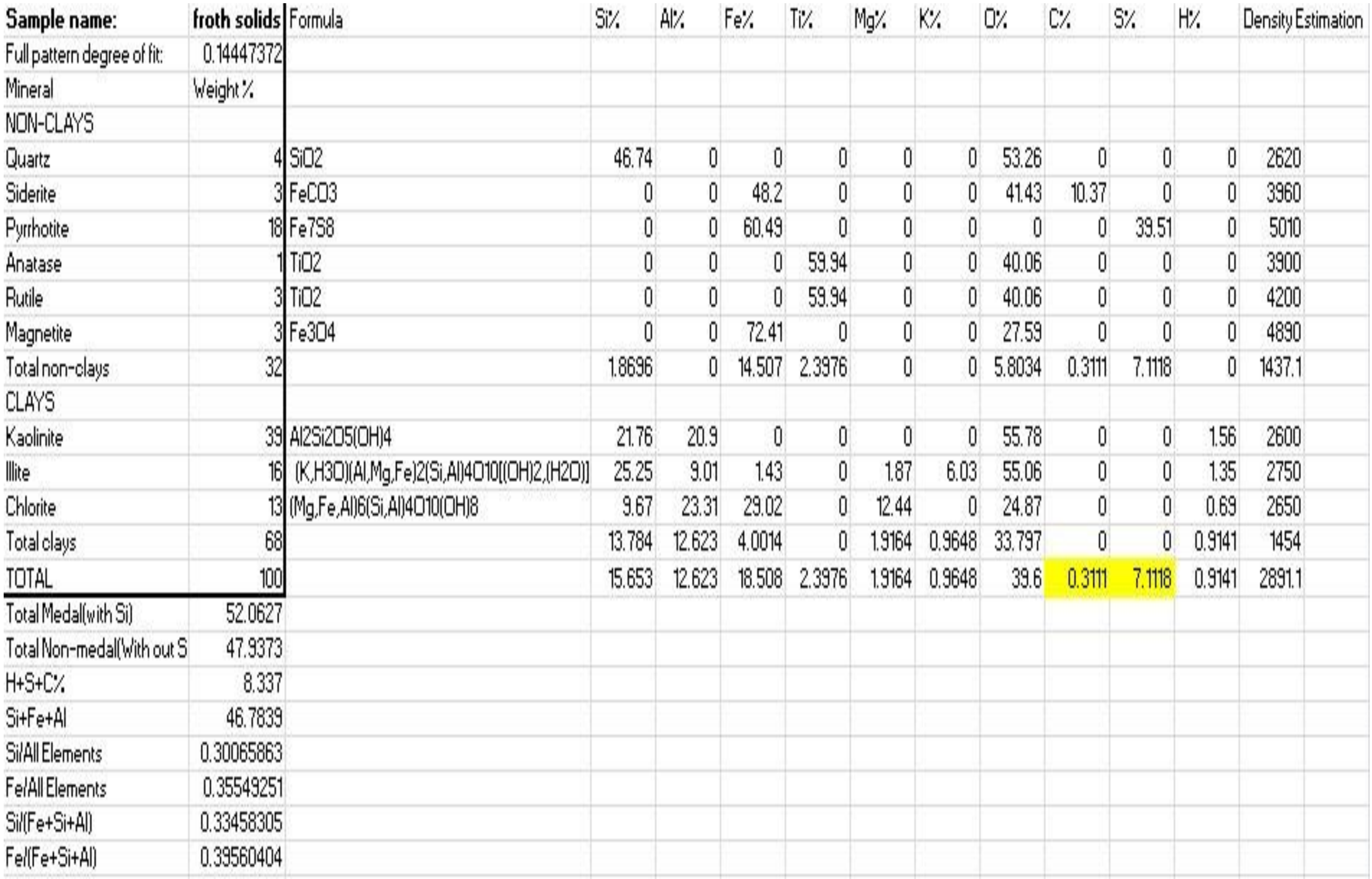
Appendix C Sample Calculation of Organics

Spread Sheet: Mineral composition of fines before reaction



Sample name:	froth solids	Formula	Si%	Al%	Fe%	Ti%	Mg%	K%	O%	C%	S%	H%	Density Estim.
Full pattern degree of fit:	0.14447372												
Mineral	Weight %												
NON-CLAYS													
Quartz	5	SiO2	46.74	0.00	0.00	0.00	0.00	0.00	53.26	0.00	0.00	0.00	2620
Siderite	19	FeCO3	0.00	0.00	48.20	0.00	0.00	0.00	41.43	10.37	0.00	0.00	3960
Pyrite	6	FeS2	0.00	0.00	46.55	0.00	0.00	0.00	0.00	0.00	53.45	0.00	5010
Anatase	1	TiO2	0.00	0.00	0.00	59.94	0.00	0.00	40.06	0.00	0.00	0.00	3900
Rutile	3	TiO2	0.00	0.00	0.00	59.94	0.00	0.00	40.06	0.00	0.00	0.00	4200
Total non-clays	34		2.34	0.00	11.95	2.40	0.00	0.00	12.14	1.97	3.21	0.00	1349
CLAYS													
Kaolinite	41	Al2Si2O5(OH)4	21.76	20.90	0.00	0.00	0.00	0.00	55.78	0.00	0.00	1.56	2600
Illite	17	(K,H3O)(Al,Mg,Fe)2(Si,Al)4O10[(OH)2,(H2O)]	25.25	9.01	1.43	0.00	1.87	6.03	55.06	0.00	0.00	1.35	2750
Chlorite	8	(Mg,Fe,Al)6(Si,Al)4O10(OH)8	9.67	23.31	29.02	0.00	12.44	0.00	24.87	0.00	0.00	0.69	2650
Total clays	66		13.99	11.97	2.56	0.00	1.31	1.03	34.22	0.00	0.00	0.92	1533.5
TOTAL	100		16.32	11.97	14.52	2.40	1.31	1.03	46.36	1.97	3.21	0.92	2882.5
Total Medal(with Si)	47.5417												
Total Non-medal(With out Si)	52.4583												
H+S+C%	6.1016												
Si+Fe+Al	42.8059												
Si/All Elements	0.34337645												
Fe/All Elements	0.30532564												
Si/(Fe+Si+Al)	0.38136565												
Fe/(Fe+Si+Al)	0.33910512												

Mineral composition of fines after reaction with bitumen at 392°C for 30min



Sample name:	froth solids	Formula	Si%	Al%	Fe%	Ti%	Mg%	K%	O%	C%	S%	H%	Density Estimation
Full pattern degree of fit:	0.14447372												
Mineral	Weight %												
NON-CLAYS													
Quartz	4	SiO2	46.74	0	0	0	0	0	53.26	0	0	0	2620
Siderite	3	FeCO3	0	0	48.2	0	0	0	41.43	10.37	0	0	3960
Pyrrhotite	18	Fe7S8	0	0	60.49	0	0	0	0	0	39.51	0	5010
Anatase	1	TiO2	0	0	0	59.94	0	0	40.06	0	0	0	3900
Rutile	3	TiO2	0	0	0	59.94	0	0	40.06	0	0	0	4200
Magnetite	3	Fe3O4	0	0	72.41	0	0	0	27.59	0	0	0	4890
Total non-clays	32		1.8696	0	14.507	2.3976	0	0	5.8034	0.3111	7.1118	0	1437.1
CLAYS													
Kaolinite	39	Al2Si2O5(OH)4	21.76	20.9	0	0	0	0	55.78	0	0	1.56	2600
Illite	16	(K,H3O)(Al,Mg,Fe)2(Si,Al)4O10[(OH)2,(H2O)]	25.25	9.01	1.43	0	1.87	6.03	55.06	0	0	1.35	2750
Chlorite	13	(Mg,Fe,Al)6(Si,Al)4O10(OH)8	9.67	23.31	29.02	0	12.44	0	24.87	0	0	0.69	2650
Total clays	68		13.784	12.623	4.0014	0	1.9164	0.9648	33.797	0	0	0.9141	1454
TOTAL	100		15.653	12.623	18.508	2.3976	1.9164	0.9648	39.6	0.3111	7.1118	0.9141	2891.1
Total Medal(with Si)	52.0627												
Total Non-medal(With out S	47.9373												
H+S+C%	8.337												
Si+Fe+Al	46.7839												
Si/All Elements	0.30065863												
Fe/All Elements	0.35549251												
Si/(Fe+Si+Al)	0.33458305												
Fe/(Fe+Si+Al)	0.39560404												

Sample Calculations of weight fraction of organics

For an untreated extracted fine sample:

N%: 0.31   C%:18.60   H%:1.58   S%:4.63

Assumption 1: Organics only formed by these 4 elements. Oxygen is negligible.

Assumption 2: No extra inorganic carbon except the one in siderite and no extra inorganic sulfur except the one in pyrite.

Assumption 3: empirical formulas of minerals are as shown in the table above

The number circled in red is the weight fraction of C+H+S elements in mineral

Total organics with CHS in minerals:

$(18.60+1.58+4.63)*100\%=24.81\%$

Let x=mineral wt% in the sample and y=organic wt% in the sample and assume 1g of sample

Thus: $0.2481-0.0610x=y$; $x+y=1$

Solve: $x=80\%$ and $y=20\%$

Calculation of Sulfur and Carbon content in the organics associated with fines before reaction

Total C=0.0197*0.8+Corgan*0.2=0.186

Total S=0.0321*0.8+Sorgan*0.2=0.0463

Corgan=85.1%   Sorgan=10.3%

C is very close to carbon content in asphaltene

S is higher than sulfur content in asphaltene

Calculations of Sulfur Removal due to Pyrrhotite Formation

If froth contains 10% fines. Assume 100g froth, 10g of it is fines. Based on the spread sheet, 1.9g of the fines is siderite and 0.6g of it is pyrite. Pyrite contains 0.32g of sulfur Iron is the used for material balance. Thus,

46.55%*0.6+48.2%*1.9=1.2g of Iron in the froth

After the reaction, according to the spread sheet, for all the minerals that contains iron,

12.5% is siderite 12.5% is magnetite 75% is pyrrhotite.

Iron content from each minerals:

Siderite: 48.2%*12.5%/(48.2%*12.5%+60.49%*75%+72.41%*12.5)=10.3%

Pyrrhotite: 60.49%*75%/(48.2%*12.5%+60.49%*75%+72.41%*12.5)=74.8%

Magnetite: 100%-10.3%-74.8%=14.9%

The amount of sulfur from pyrrhotite:

(74.8%*1.2g/60.49%)*(100%-60.49*)=0.59g of sulfur

The amount of sulfur from organics

0.59g-0.32g=0.21g Thus 0.21% sulfur content can be removed by fines during the reaction.

Appendix D Heating Curve of the Sand Bath

The set temperature in the reactor was 420°C and the maximum temperature it reached was about 410°C. It took about 2min for the reactor to reach the maximum temperature.

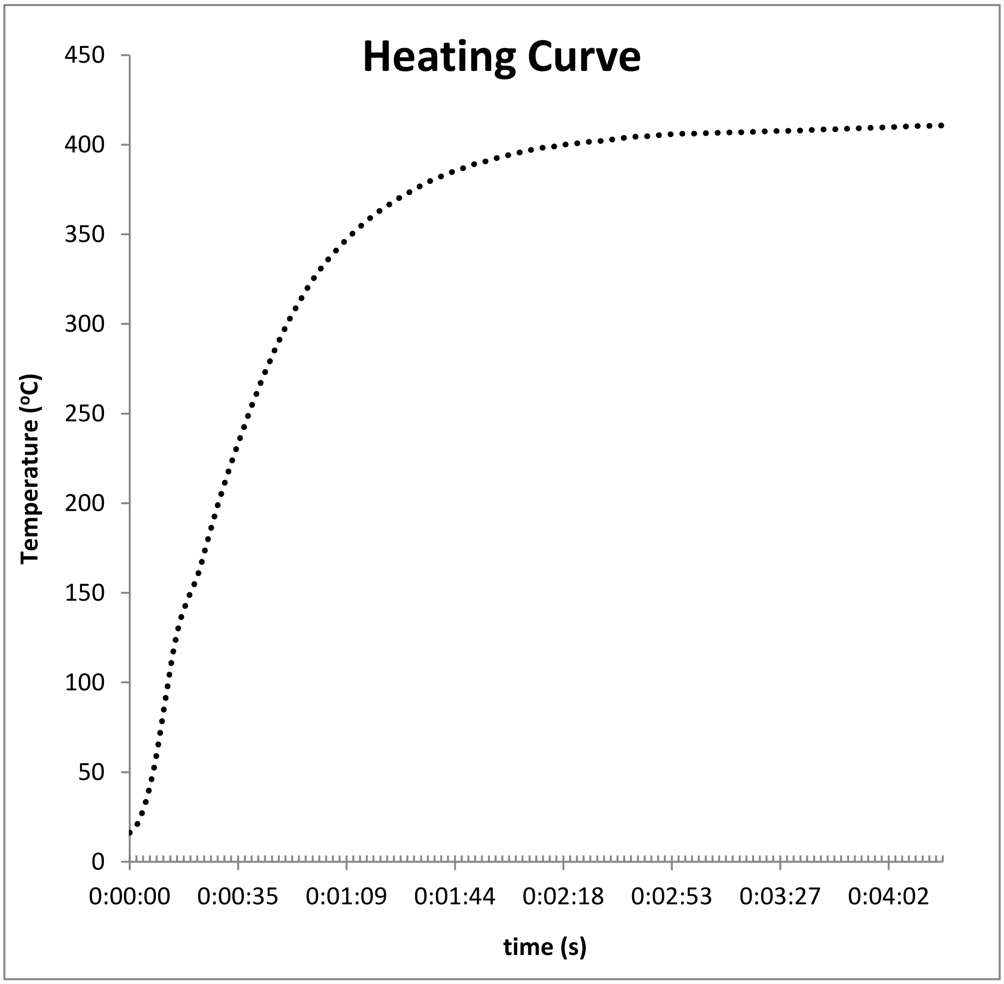


Figure D.1 Heating curve of micro reactor heated in a sand bath

Appendix E Comparison of the Particles` Chord Length Distribution after Water Droplets were Boiled Out

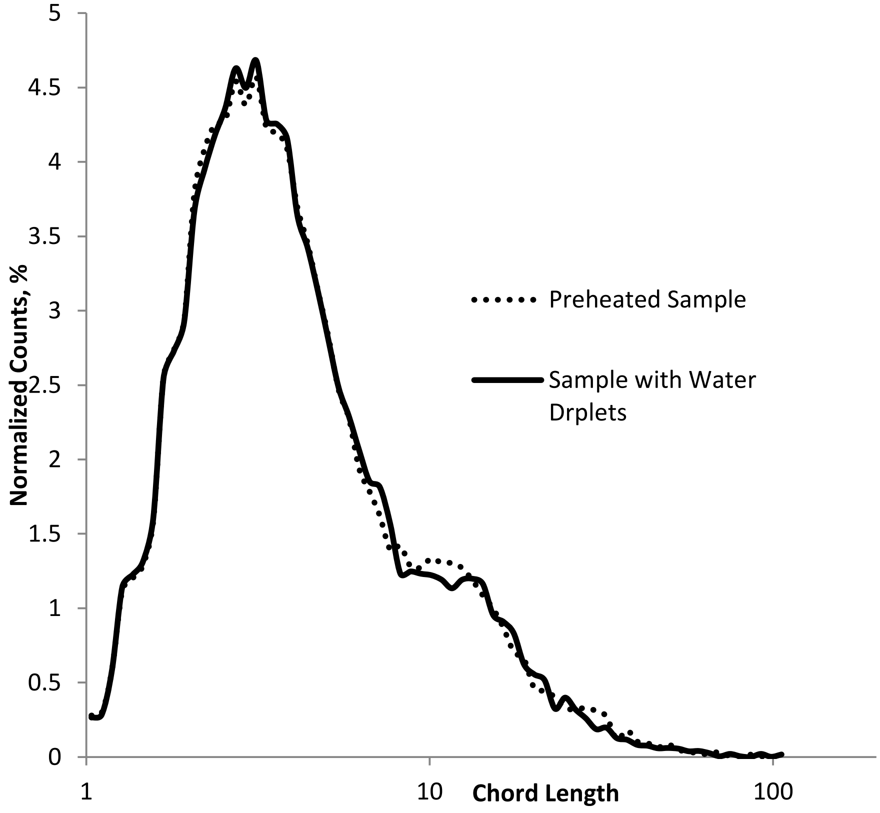


Figure E.1 Chord length distribution of fines in toluene diluted froth before and after the water was boiled out

As the figure showed, no significant changes had taken place to the particles if the water was boiled out or not. The water droplets contributed too few counts to affect the results.

Appendix F Estimate of wt% of Organics in Fines by Ashing

Another QXRD run was carried out to check the mineral composition of the fines. Since illite, kaolinite, and chlorite shared many peaks in XRD patterns, very little chlorite was found this time. According to the TGA curve, over the temperature range from 60°C-80°C, there was a slight weight loss of 1.56wt%. No further temperature until 140°C was reached. I assume that the initial weight loss was due to dehydration. The left over 98.44% sample was normalized to 100% of organics+ minerals. Finally, 68.18 wt% of the sample was left after 800°C Treatment. Sample was hold at 800°C for 20min. During the 20min, only 0.14% weight was lost. Thus 31.82% weight was lost during the air oxidation.

According to P.K.GALLAGHER (1981), under sufficient air supply, siderite will have the following reaction at about 600°C:

$2FeCO_3+1/2O_2=Fe_2O_3+2CO_2$

31% weight was lost during the process

And for Pyrite:

George-Maria(1947) Stated at more than 500°C under air flow:
$FeS_2+11/4O_2=l/2Fe_2O_3+2SO_2$
33% weight was lost during the process

Kaolinite will lose about 12% of its weight according to previous TGA study

Illite only lose 4% according to Euigyung Jeong (2011)

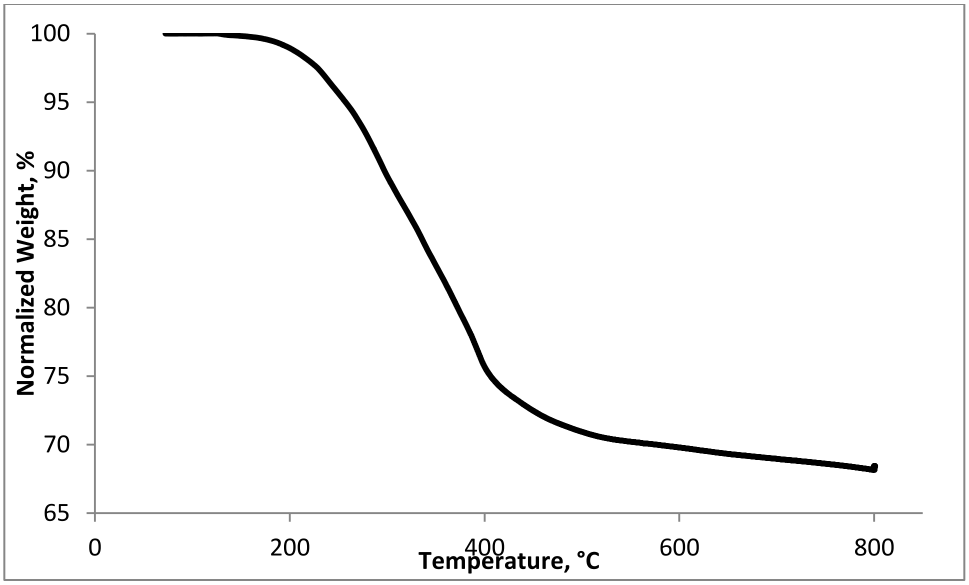


Figure F.1 TGA curve of kaolinite heated in air

Calculate according to the XRD results.

(0.27*0.94+0.38*0.88+0.2*0.69+0.06*0.67+0.09)*100%=85.6%

Assume only the above four species would be affected by air oxidation. Thus,

68.18%/85.6%*100%=79.65%

The organic weight percentage:

100%-79.65%=**20.35%**