I am soaring high
Always high, flying, flying…
Like the proverbial phoenix
Risen from the ashes
I shall overcome every obstacle
With God's guidance

I will not go down
Always, will I fly high, high…
Towards heaven above
Until I have achieved all
Accomplished everything

I was born to do
I look forward
Always, to that great reward, paradise, paradise …
To praise Him who made me
Praise Him forevermore

University of Alberta

Characterization of Solids Isolated from Different Oil Sand Ores

by

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Dedication

This thesis is dedicated to God the Father, God the Son and God the Holy Spirit.

Without Him, this written work would not have been possible.

Also, to my mother Mary, all saints and angels in heaven: for interceding to our Lord Jesus Christ on my behalf.

Abstract

Understanding mineralogy and surface properties of fine solids is vital in oil sands processing and tailings management. Fine solids in oil sands are often contaminated by tightly bound organic matter (OM) originally or during hydrocarbon removal, thereby increasing surface hydrophobicity and making its characterization problematic. The surface properties of solids affect the entire process cycle of obtaining synthetic crude oil from surface-mined oil sands using a water-based extraction process, and managing produced tailings.

In this study, low temperature ashing (LTA) was found to be a more suitable method than hydrogen peroxide (H_2O_2) for OM removal from clay sized minerals (CSM) because of its selectivity for decomposing only organics. The mineralogy and cation exchange capacity of the CSM remained unaffected after treatment with LTA as opposed to H_2O_2 treatment.

To comprehend the organo-mineral interactions in oil sands, solids isolated from weathered and oil sands having low- and high-fine solids content were examined. Low-fines ore possessed the lowest amount of organic coated solids and highest bitumen recovery. The solids in the bitumen froth from these ores were of less quartz, more carbonates, transition metals and carbon than the solids in the corresponding tailings. Infrared spectra showed a likely association between OM and carbonates in the organic coated solids isolated from bitumen froth.

Weathered ores were found to contain more organic coated solids which were observed to reduce bitumen recovery from these oil sands ores.

A further study of weathered ores was undertaken to understand the reason for its poor processability from a mineralogical perspective. A higher amount of divalent cations was found in weathered ores than in high- and low-fines ores. The low-fines ore was found to exhibit the highest kaolinitic to illitic mineral ratio, while the high-fines ore displayed the lowest ratio. Siderite and pyrite were observed in the solids isolated from weathered and high-fines ores, but were absent in low-fines ores. In addition to wettability, the poor processability of weathered ores appeared to be related to the interactions between the divalent cations and illite, and the cementation effect of the siderite concretions on the oil sand grains, which inhibited bitumen liberation. Corrensite, a mixed-layer chlorite-vermiculite, was detected for the first time in weathered ores.

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NOMENCLATURE

CSM – clay-sized minerals

CW1OF, CW2OF, CW3OF, CGOF and CPOF – isolated solids (clay fraction) from bitumen froth

CW1OT, CW2OT, CW3OT, CGOT and CPOT– isolated solids (clay fraction) from tailings

CDW1, CDW2, CDW3, CDP and CDG – isolated solids (clay fraction) from the Dean Stark Apparatus

COW1F, COW2F, COW3F, COPF and COGF – organic wet isolated solids (clay fraction) from bitumen froth

COW1T, COW2T, COW3T, COPT and COST– organic wet isolated solids (clay fraction) from tailings

CWW1F, CWW2F, CWW3F, CWPF and CWGF – aqueous wet isolated solids (clay fraction) from bitumen froth

CWW1T, CWW2T, CWW3T, CWPT and CWGT – aqueous wet isolated solids (clay fraction) from tailings

CEC – cation exchange capacity

CuTrien – copper triethylenetetramine

DRIFTS – diffuse reflectance infrared spectroscopy

DV and DVA – untreated and LTA treated model clays

DW1, DW2, DW3, DP and DG – Overall isolated solids from the Dean Stark Apparatus

EDX – energy dispersive x- ray spectroscopy

FA, FB and FC – untreated, LTA treated and H_2O_2 treated CSM from bitumen froth

G and P – low and high fines oil sands ore, respectively

IR – Infrared

LTA – low temperature ashing

MB – methylene blue

MIF – mineral intensity factor

OM – organic matter

OW1F, OW2F, OW3F, OPF and OGF– organic wet isolated solids from bitumen froth

OW1T, OW2T, OW3T, OPT and OGT– organic wet isolated solids from tailings

PSD – particle size distribution

RF – radio frequency radiation

SA – surface area

SDW1, SDW2, SDW3, SDP and SDG – isolated solids (silt fraction) from the Dean Stark Apparatus

SEM – scanning electron microscope

SW1OF, SW2OF, SW3OF, SGOF and SPOF – isolated solids (silt fraction) from bitumen froth

SW1OT, SW2OT, SW3OT, SGOT and SPOT– isolated solids (silt fraction) from tailings

SWW1F, SWW2F, SWW3F, SWPF and SWGF – aqueous wet isolated solids (silt fraction) from bitumen froth

SWW1T, SWW2T, SWW3T, SWPT and SWGT – aqueous wet isolated solids (silt fraction) from tailings

TA, TB and TC – untreated, LTA treated and H_2O_2 treated CSM from tailings

W1, W2 and W3 – weathered oil sands ore

W1OF, W2OF, W3OF, GOF and POF – isolated solids from bitumen froth

W1OT, W2OT, W3OT, GOT and POT– isolated solids from tailings

WW1F, WW2F, WW3F, WPF and WGF – aqueous wet isolated solids from bitumen froth

WW1T, WW2T, WW3T, WPT and WGT – aqueous wet isolated solids from tailings

XRD – x-ray diffraction

CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

This chapter introduces oil sands, presents the justification, objectives and outline of this thesis. The general background on soil and clay mineralogy is discussed. Previous research studies on solids isolated from oil sands and the techniques used in their characterization are also presented.

1.1 Introduction

Oil sands comprise of silica sand and other minerals impregnated with bitumen at varying concentrations. Oil sands deposits are located in the Athabasca, Cold Lake and Peace River regions of Northern Alberta, Canada. This deposit was first documented by a fur trader, Peter Pond in 1778[1] and commercialization to obtain synthetic crude oil from the extracted bitumen commenced in 1967[1]. As of year 2007, the total in-situ and mineable reserves for crude bitumen in Alberta was estimated at 173 billion barrels[2].

Oil sands ores are generally classified by their bitumen content. This could be high grade ore of over 12 wt.% bitumen, average grade ore characterized by 9 to 12 wt.% bitumen and low grade ore of less than 9 wt.% bitumen. A high bitumen recovery is usually obtained from the high grade ore but this is seldom the case for one type of ore [3-16] described as being “weathered”, “oxidized” or “degraded”. This type of ore usually has a high bitumen content (>12 wt.%), low fines (< 45 µm) content and portrays a low bitumen recovery.

Bitumen is produced from oil sands by either warm water – based extraction of surface-mined oil sands or by in-situ techniques. Major oil sands operating companies such as Suncor Energy Inc., Syncrude Canada Ltd., Shell Albian Sands and Canadian Natural Resources Ltd. depend on surface mining extraction method for producing bitumen from oil sands. In-situ techniques are usually employed for deep deposits where overburden removal can be an economic graveyard[1]. The water-wet property of the sand grains makes the water-based process of extracting bitumen from oil sands possible. Without this characteristic, the recovery of bitumen would be tremendously difficult.

In surface mining oil sands operations, over 70% of the water utilized in the water based process is re-used while the remaining 30% is trapped in slow-settling tailings ponds[17] containing mostly fine solids (<45 µm). Hence, the challenges posed by the water based process are the effective recovery of bitumen from the sand grains of ores and the management of the slow-settling waste tailings material that is currently stored in giant ponds, which has become a major environmental issue[1]. Consequently, understanding mineralogy and surface properties of oil sands fine solids (<45 µm) is vital in oil sands processing as well as in modeling tailings behavior.

Furthermore, organic matter (OM), which is insoluble in common organic solvents, such as toluene and isopropyl alcohol, is often associated with fines fraction (<45 µm) of particulate minerals present in oil sands[18-20]. This OM makes the solid surface hydrophobic[21], permitting particle bridging by the adsorption of residual bitumen. The presence of these *hydrophobic* solids has been linked to poor bitumen froth quality, fouling of bitumen upgrading equipment and poor compaction of the fine grained sludge in tailings slurry[21-28]. This further justifies the need for studying organo-mineral interactions in oil sands.

Moreover, in view of the fact that a great deal of information about the character of many oil sands ore type / deposit is lacking, the objective of this study is to characterize different types of oil sands ores (weathered, high and low fines) predominantly from a mineralogical perspective in order to establish their relationship to their processability. Organic coated solids isolated from the bitumen froth and tailings after a warm – water based extraction process with a Denver flotation cell were analyzed. This would enable us to understand the interactions of organic matter with minerals and their effect on oil sands processability.

1.2 Thesis Outline

This Thesis has been divided into six chapters:

CHAPTER ONE: This chapter introduces oil sands, presents the justification, objectives and outline of this thesis. The general background on soil and clay mineralogy is discussed. Previous research studies on solids isolated from oil sands and the techniques used in their characterization are reviewed.

CHAPTER TWO: This chapter presents the experimental work of this study. The materials, experimental procedures and techniques including the operating conditions are described.

CHAPTER THREE: This chapter presents pre-treatment methods of solids isolated from oil sands, which has been published in the *Energy and Fuel*.

CHAPTER FOUR: This chapter presents the characterization of organic coated solids isolated from different oil sands, which is in press with the *Canadian Journal of Chemical Engineering*.

CHAPTER FIVE: This chapter presents the characterization of weathered oil sands ores, which is submitted to *Applied Clay Science* for consideration of publication.

CHAPTER SIX: This chapter presents the overall conclusions from this investigation. The contributions of the findings of this investigation to the oil sands industry are itemized and recommendations for future work are presented in this chapter.

1.3 General Background

1.3.1 Soil

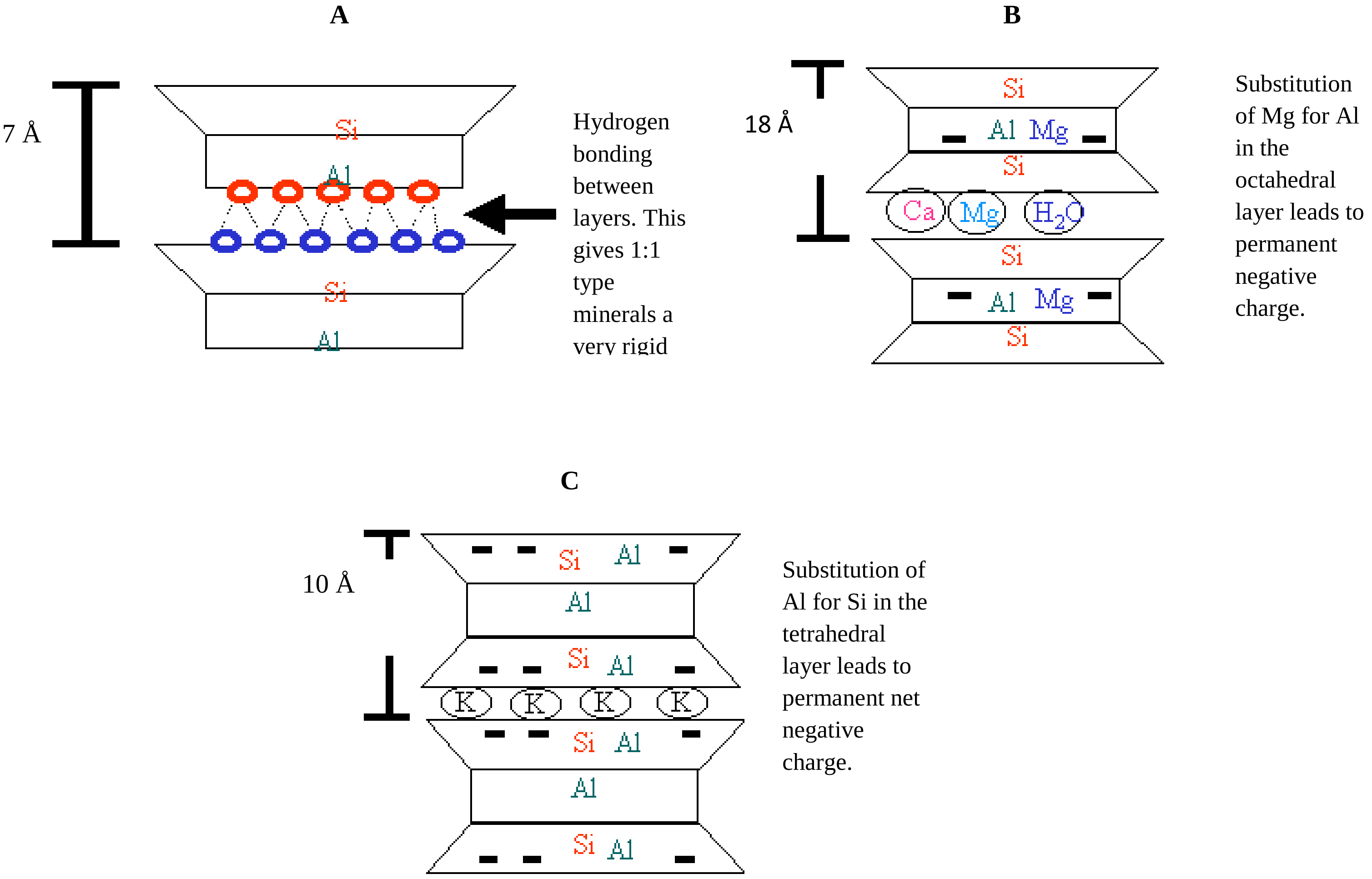
Soil can be defined as the unconsolidated, thin, changeable layer of mineral and organic material which is usually biologically active. The soil covers most of the earth's land surface[29]. It originates from a consolidated rock or unconsolidated material deposited by wind / water and inherits the mineral types found there. Soils consist of two major components[30] – minerals derived from the weathering of rocks such as igneous, sedimentary and metamorphic rocks of the earth's crust; and organic materials derived from plants and micro-organisms.

Weathering involves the dissolution and reformation of new minerals when rocks are exposed to water, air and organisms[29]. The weathered rock is usually referred to as the parent material in which the mineral soils form. Soils may also contain the unweathered mineral residuals from the parent material as well as the minerals that weathering produces[29]. The major weathering products are the clay minerals which stick to one another and other particles. These clay minerals usually retain water, organic compounds and plant nutrients on their surfaces[29]. They are platy-like and "*surface active*" due to their large surface area per unit volume. Their size[29] is usually less than 2 µm, in contrast to other solids in the soil – silt (0.2 µm to 50 µm) and sand (50 µm to 200 µm).

1.3.2 Clay Mineralogy

According to Giese[31], clay is a solid that exhibits plastic behavior when mixed with water while clay minerals are materials, which have a layer structure or a structure substantially derived from or containing major features of such layer structures. A study of the crystal structure of clay is important in understanding its physical and chemical properties since the interfacial properties of solids are related to the arrangement of the atoms at and near the external surface of crystals[31]. A defect in the stacking of the crystal layers could contribute to the nature of its physical properties: regular-perfect structure in most *kaolinite*; and weak-diffuse structure in *halloysite*[31].

Clay minerals are made up of polymerized polyhedral layers with an interlayer separating them. The polyhedral layers consist of tetrahedral (silicon and oxygen) and octahedral (aluminum / magnesium and oxygen / hydroxyl) sheets[31, 32]. The arrangement could be 1:1 – tetrahedral (T) + octahedral (O) layers; or 2:1 – tetrahedral + octahedral + tetrahedral (T-O-T). The 2:1 structures could be trioctahedral – when each oxygen atom is coordinated with three divalent cations such as magnesium and ferrous iron (Fe^{2+}) or dioctahedral – when each oxygen atom is coordinated with two trivalent cations such as aluminium and ferric iron (Fe^{3+}). Figure 1.1 depicts these structural arrangements as seen in the Lecture notes (8) of Jodi Johnson – Maynard[33].



Hydrogen bonding between layers. This gives 1:1 type minerals a very rigid

Substitution of Mg for Al in the octahedral layer leads to permanent negative charge.

Substitution of Al for Si in the tetrahedral layer leads to permanent net negative charge.

Figure 1.1: Types of Clay Mineral Structures – **A:** 1:1Clay[33] (Kaolinite), **B:** 2:1 Expanding Clay[33] (Smectite group) and **C:** 2:1 Non-Expanding Clay[33] (Illite).

Another arrangement could be 2:1:1 / 2:2 layer structures as seen in *chlorite* and some *vermiculite* in which a hydroxide (magnesium-octahedral) sheet occupy the interlayer space[32]. As seen in Figure 1.1, most common interlayer cations are potassium (*K*), sodium (*Na*) and calcium (*C*a). Other materials that could fill the interlayer space are organics and water in the case of most *smectites* and *vermiculites* which are expanding clays, i.e., they expand when they absorb water into their interlayer space.

The properties of clay minerals that make them important to soils are the large surface area to volume ratio and charge[29]. Due to the large surface area to volume ratio, clay minerals have highly reactive surfaces including cation exchange capacities and catalytic activity[31]. While the net effect of the presence of edges and isomorphous substitution, on the other hand enables clay minerals to possess a net negative and sometimes positive charge[29]. Due to these charges, positively-charged cations (*K*, *Na*, *Ca*) and organic compounds are able to attach to the clay minerals even though not held too tightly[29].

The charges that occur in clay mineral structures are caused by:

1. Isomorphous substitution: when Al^{3+} cation replaces the Si^{4+} cation in the tetrahedral sheet or Mg^{2+} cation replaces the Al^{3+} cation in the octahedral sheet. The cation being replaced often has an equal or higher positive charge to that replacing it. For instance, trivalent cations would be

replaced by another trivalent cation and if this is absent, a divalent cation would replace it, leading to a charge imbalance. The exception to this is when a clay mineral selectively prefers a certain monovalent cation to the divalent cation present[30]. This can be observed in illite, which will be discussed in the subsequent paragraph. The resulting charge from isomorphous substitution is often referred to as *fixed*, *permanent* or *lattice* charge[29,32].

2. Edge charge where the crystals end: this charge is a function of the pH of medium in which the clay minerals are immersed[29,32]. This is a consequence of the protonation or deprotonation of the oxides and hydroxides of crystalline or amorphous clay minerals[29]. This is very important as changes in pH and net charge control dispersion and flocculation of clays[32].

Layer charges are important since they are used as a criterion for clay classification and they also control how the clay minerals interact with the environment (especially the 2:1 clay minerals).

Organic compounds interact with clay minerals[32] in the following ways:

1. They are attracted to the charge of *siloxane* surfaces exposed in the interlayer space of 2:1 clay minerals.

2. Neutral organic molecules could be adsorbed by forming complexes with transition metal cations that have previously been introduced.

This interaction is important in understanding the formation of, exploration for and recovery of petroleum[32] and in the role that clay minerals play in prebiotic syntheses and storage of molecules of biological interest.

The most common clay minerals encountered in oil sands are *kaolinite, illite, smectite, chlorite* and mixed-layer clays of the aforementioned clay minerals. Kaolinite is a 1:1 clay mineral with a basal (001) spacing of 0.7 nm. The 1:1 arrangement permits the stacked layers of T-O to be bound together by hydrogen bonding[30]. This makes the structure of kaolinite to be rigid and non-expanding[30]. Hence, water and cations cannot occupy its interlayer space. Moreover, this makes the surface area of kaolinite to be limited to its external surface and consequently limits its cation exchange capacity[30] (CEC). CEC is very important and is a measure of the ability of a clay mineral to adsorb exchangeable cations. The isomorphous substitution in kaolinite is rather limited and this results in its relatively low net negative charge[30]. Another source of charge in this clay mineral is deprotonation or protonation of its exposed hydroxyl edges, which is dependent on the pH of the environment[30].

Illite and smectite are both 2:1 clay minerals with basal (001) spacings of 1.0 nm and between 1.0 to 2.0 nm, respectively. Isomorphous substitution in illite occurs mainly in the tetrahedral sheets and is its main source of negative charge[30]. This negative charge attracts cations, with a high selectivity for potassium (K^+). According to Brady and Weil[30], this preference is due to the fact that potassium ions fit snugly into certain spaces (hexagonal holes) that exist between the tetrahedral oxygen groups. This is illustrated in Figure 1.1. Due to the presence of the potassium ions, which is strongly attracted to the negative charge caused by isomophous substitution, a strong bound occurs between adjacent tetrahedral sheets in this 2:1 clay mineral[30]. This makes illite to be non-expanding like the previously discussed kaolinite[30].

Unlike illite, smectites are expanding clay minerals due to the lack of strong bonds within its structure. The lack of a strong bound is because the T-O-T stacking does not make hydrogen bonding possible as seen in kaolinite and there are no snugly fitted potassium ions in its tetrahedral sheet as in illite[30]. This makes smectite have a high internal surface area in addition to its exposed external surface area. The expansive property of smectite permits the occupancy of cations, water and organics in its interlayer. Furthermore, isomorphous substitution in both the tetrahedral and octahedral sheets of this clay mineral results in high negative charge and leads to high CEC[30].

Chlorite, a 2:1:1 or 2:2 clay mineral has a basal (001) spacing of 1.4 nm. It is non-expansive because of the presence of hydrogen bonding within its structure. As the structure is T-O-T-H (H refers to the Mg-octahedral (magnesium-hydroxide sheet), there is hydrogen bonding between the hydroxide and tetrahedral sheets[30]. This makes chlorite to be quite similar to illite in terms of colloidal properties[30] as seen in Table 1.1.

1.3.2.1 Properties of Major Clay Minerals

As cited earlier, clay minerals are a product of weathered rocks and the amount of a particular type of clay mineral reflects the degree of weathering or diagenesis that has taken place in the soil. According to Brady and Weil[30], mild weathering encourages the formation of 2:1 types of clay minerals such as fine-grained mica (illite), vermiculite and smectite, while intense weathering destroys these clay minerals. The end products of highly weathered soils are kaolinite, aluminium and iron oxide clays[30]. Properties of some of the quoted clay minerals are presented in Table 1.1.

1.3.3 Previous Research on the Characterization of Solids in Oil Sand Ores

A summary of the previous research on characterization of solids[23, 24, 26, 34-55] in oil sands is presented in Table 1.2. It contains a list of research findings related to the characterization of solids from oil sands. The sample type, techniques utilized, and conclusions reached from these studies are summarized in Table 1.2.

1.3.3.1 Characterization Techniques

As seen in Table 1.2, the technique used in the characterization of solids depends on the physical / chemical property of interest. The techniques that are employed

Table 1.1: Major Clay Minerals' Properties[30]

Clay Mineral	**Size (μm)**	**Surface Area (m^2/g)**		**Interlayer Spacing (nm)**	**Cation Sorption (meq/100 g)**
		External	**Internal**		
Kaolinite	0.1-5.0	5-30	-	0.7	1-15
Smectites	<1.0	80-150	550-650	1.0-2.0	80-150
Vermiculite	0.1-5.0	70-120	600-700	1.0-1.5	100-200
Illite	0.2-2.0	70-175	-	1.0	10-40
Chlorite	0.1-2.0	70-100	-	1.4	10-40

are the x-ray diffraction analysis (XRD) and the infrared methods for identification and quantification of clay minerals; transmission electron microscopy (TEM) / scanning electron microscopy (SEM) for studying the high resolution morphology of the solids; x-ray fluorescence spectroscopy for the quantitative and qualitative determination of elements in a sample; and nuclear magnetic resonance spectroscopy (NMR) for studying the structural components of clay minerals and to probe the identity as well as the physical properties of any liquid phase molecules associated with clay minerals. NMR is used in the detailed chemical characterisation of organic molecules that are either weakly adsorbed on clay surfaces or intercalated into the interlayer spaces.

The following techniques were used in this study:

1. Scanning electron microscopy (SEM) for studying the morphology of solids.

2. Scanning electron microscopy (SEM) coupled with energy dispersive analysis by x–rays (EDAX) for semi – quantitative analysis of elements present in a sample.

3. X-ray diffraction (XRD) for identifying and quantifying clay sized minerals and silt.
4. Fourier transform infrared spectroscopy (FTIR) which provides the functional group information of organic and inorganic compounds.

5. Elemental analyser for determining the total carbon, hydrogen, nitrogen and sulphur content in a sample.

Table 1.2: Summary of Previous Research on Solids Characterization from Oil Sands

SN	Author	Year	Sample Type	Technique Applied	Solids Characterized		Conclusion
					Clay Minerals	**Organic Matter**	
1	Bayliss et al.[34].	1976	343 samples from different oil sands reserves	XRD	Yes	No	* Expandable clay minerals must be avoided when using in-situ techniques in oil sands extraction[34]. * Observed the presence of montmorillonite in oil – poor sands.
2	Camp[35]	1976a	Tailings pond sample from Great Canadian Oil Sands Limited (now Suncor)	N/A	Yes	No	Behaviour of process tailings upon disposal is dependent on the quantity and presence of clay minerals[35].
3	Camp[36]	1976b	Tar sand samples from different reserves	N/A	Yes	No	Identified some clay minerals in tar sands.

SN	**Author**	**Year**	**Sample Type**	**Technique Applied**	**Solids Characterized**		**Conclusion**
					Clay Minerals	**Organic Matter**	
4	Yong et al.[37].	1978	Tailings pond sample from Great Canadian Oil Sands Limited (Suncor)	N/A	Yes	No	Dynamic equilibrium status of the tailings sludge is controlled by the mineral particle interaction within the environment[37].
5	Kessick[38]	1979	Tailings pond sample from Great Canadian Oil Sands Limited (Suncor)	XRD	Yes	No	Absence of swelling clays promotes gel- formation in oil sands clay slime that is necessary for dewaterability[38].
6	Duesseault et al.[39].	1979	83 specimens of basal McMurray formation Clay Shale (*Basal Clay)*	XRD	Yes	No	*Presence of basal clay[39] in extraction processes and the resulting tailings stream would be deleterious to settling and consolidation in tailing ponds. * Basal clay's behaviour is

SN	Author	Year	Sample Type	Technique Applied	Solids Characterized		Conclusion
					Clay Minerals	**Organic Matter**	
							intermediate to that of smectite and kaolinite[39].
7	Roberts et al.[40].	1980	Suncor Tailings pond samples	XRD	Yes	Yes	An attempt at correlating the clay minerals in different samples to solve the problem of tailings sludge disposal.
8	Ignasiak et al.[41].	1983	Sample from Soxhlet Extraction	XRD, Infrared & Inductively Coupled Argon Plasma	Yes	Yes	Observed a decrease in the crystallinity of clay minerals as particle size diminished[41].
9	Kotlyar et al.[23].	1984	Low grade Oil Sands (5- 10 wt. % bitumen) from Alberta Research Council Sample	XRD, D.C. Arc Emission Spectrometer, X- Ray Fluorescence Spectrometer &	Yes	Yes	* Organic matter[23] may be bound to metal oxides and hydrous oxides, which may coat the surface of clay minerals.

SN	Author	Year	Sample Type	Technique Applied	Solids Characterized		Conclusion
					Clay Minerals	Organic Matter	
			Bank	Infrared			* Siderite could be the major inorganic component in residual organic-mineral association[23] * Organic matter increased with a decrease in particle size[23].
10	Ignasiak et al.[42].	1985	- Syncrude Beach Sand - SBS (6.1 wt. % bitumen) - Syncrude High Grade Oil Sand - SHG (11.8 wt. % bitumen)	XRD & Infrared	Yes	Yes	* No major difference found between the 2 samples in terms of mineral composition and surface area[42]. * SBS richer in fines and darker * Iron plays a major role in organic mineral-

SN	Author	Year	Sample Type	Technique Applied	Solids Characterized		Conclusion
					Clay Minerals	Organic Matter	
							interaction[42].
11	Kotlyar et al.[43].	1985	- Syncrude high grade ore (11-15.6 wt. % bitumen) - Syncrude medium grade ore (9.5 wt. % bitumen) - Syncrude low grade ore (6.7-7.9 wt. % bitumen)	XRD, D.C. Arc Emission Spectrometer, & Carbon Analyzer	Yes	Yes	Ease of bitumen separation[43] is dependent on the strength of the bonds between bitumen and the inorganic matter-humic complexes; and between the complexes and some minerals.
12	Scott et al.[44].	1985	Tailings pond sample from Syncrude	*N/A*	Yes	No	Study of clay mineral behaviour in the presence of bitumen is important in the settling and consolidation of tailings

SN	Author	Year	Sample Type	Technique Applied	Solids Characterized		Conclusion
					Clay Minerals	Organic Matter	
							solids[44].
13	Kotlyar et al.[24].	1987	3 different oil sands grade from Alberta Research Council Sample Bank and Syncrude	XRD, D.C. Arc Emission Spectrometer, & SEM	Yes	Yes	Presence of hydrophobic globules inhibits bitumen separation from oil sands[24].
14	Duesseault et al.[45].	1989	Clearwater formation overburden and tailings / mine waste	XRD	Yes	No	Blending of overburden with sludge could solve the problem of sludge disposal and smectite overburden disposal[45].
15	Kotlyar et al.[26].	1990	Oil sands of estuarine and marine origin from Syncrude	XRD, Si - NMR, TEM, X-Ray Fluorescence Spectrometer &	Yes	Yes	Clay minerals could interact with humic matter via an organic anion acting as a ligand to a metal ion, Coulombic and Van der

SN	Author	Year	Sample Type	Technique Applied	Solids Characterized		Conclusion
					Clay Minerals	Organic Matter	
				Infrared			Waal forces; and hydrogen bonding[26].
16	Ripmeester et al.[46].	1993	Tailings sample	H – NMR & O - NMR	Yes	No	Time-scale for sol-gel formation depends on solids concentration and water chemistry[46].
17	Kotlyar et al.[47].	1993	Suncor fine tails	XRD, Si - NMR, TEM & XPS	Yes	Yes	Kaolinite and mica are the main crystalline components of the colloidal solids in the oil sands fines tailings[47].
18	Cloutis et al.[48].	1995	Oil sands from Syncrude and Suncor	XRD & Diffuse Reflectance Spectroscopy (DFR)	Yes	No	DFR is a good technique for identifying clay minerals and siderite[48].
19	Kotlyar et	1995	Suncor fine tails	XRD, H - NMR,	Yes	Yes	Ultrafine solids in tailings

SN	Author	Year	Sample Type	Technique Applied	Solids Characterized		Conclusion
					Clay Minerals	**Organic Matter**	
	al.[49].			TEM, Photon Correlation Spectroscopy (PCS) & XPS			exhibit biwetted characteristics. This may be due to organic compounds coating their surface[49].
20	Omotoso et al.[50].	2002	Suncor and Syncrude fine tails	XRD	Yes	No	High surface area of the fine tailings stream could be ascribed to the interstratification of very fine illite and kaolinite with smectite[50].
21	Omotoso et al.[51].	2004	Matured fine tailings from Syncrude pond	XRD	Yes	No	High surface area of the fine tailings stream could be due to the presence of amorphous oxides[51].
22	Wallace et al.[52]	2004	Oil sands from different leases	XRD & Ion Chromatography	Yes	No	Coagulation of fines solids decreases bitumen

SN	Author	Year	Sample Type	Technique Applied	Solids Characterized		Conclusion
					Clay Minerals	**Organic Matter**	
							recovery[52].
23	Omotoso et al.[53].	2005	Oil sands from 3 different leases	XRD, Scanning Transmission X-Ray Microscopy (STXM)	Yes	No	STXM and XRD are useful for probing mineral-organic interactions in oil sands[53].
2 4	Kaminsky et al.[54].	2006	Oil sands ore from Suncor	Electron Diffraction & TEM	Yes	No	Obtaining the fundamental particle sizes of clay minerals in oil sands[54]. tailings.
25	Kaminsky et al.[55].	2009	Low grade ore from Suncor	XRD	Yes	No	Identified clay minerals from middlings, tailings and froth[55].

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CHAPTER TWO

MATERIALS AND METHODS

This chapter presents the details on the materials and methods used in the experimental work of this study.

2.1 Oil Sands

Three different oil sand ores with varying degrees of weathering are studied. For control measures, they are compared with a low- and high-fines oil sand ores. The weathered ores labeled as “W1” and “W2” are from Suncor Energy Inc. and “W3” from Syncrude Canada Ltd., while the low fines ore “G” is from Suncor Energy Inc. and high fines ore “P” from Syncrude Canada Ltd.

2.2 Oil Sands Assay

The composition of the oil sands was determined using a Dean Stark apparatus shown in Fig. 2.1. The apparatus is used for separating bitumen and formation water from solids. It consists of a heater and a round bottom – flask connected to a condenser with a trap / receiver.

For each analysis, 50 g of oil sands samples were placed into three different thimbles. Each thimble was placed in a wire mesh which was inserted and held in the neck of the flask containing approximately 200 mL of pure toluene. The flask was placed in a bowl-like heater and connected to a condenser with a graduated trap / receiver. The cold water was allowed to flow through the heat exchanger

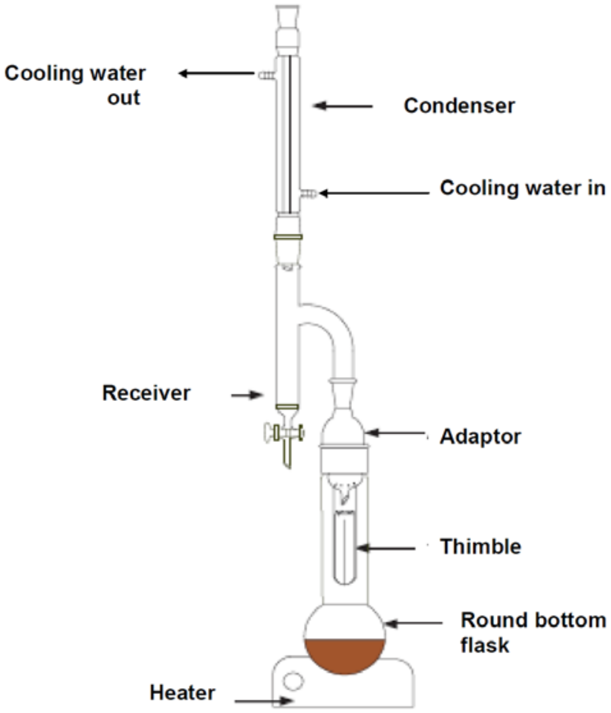

Figure 2.1: Set-up of a Dean Stark Apparatus

and condenser to condense the steam and toluene vapour. The heater was switched on to vaporize the liquids, which reflux through the oil sands sample. The reflux continued for 30 minutes at which the dripping toluene became colorless. During refluxing, the formation water in the oil sands samples also vaporises, and is collected in the graduated receiver/trap after being condensed in the condenser. At the end of the refluxing, the bitumen-free solids in the thimbles were placed in a vacuum oven to dry for over twelve hours.

The diluted bitumen in the Dean Stark flask was poured into a 250 mL round-bottom flask in which pure toluene was added to reach the 250 mL mark. The round-bottom flask was then shaken and 5 mL of the bitumen-toluene mixture was sprayed onto a precisely weighed filter paper. This filter paper was left to dry for about 25 minutes to ensure the complete evaporation of the toluene in diluted bitumen. The filter paper was subsequently weighed and the initial weight was subtracted from the final weight. The result was multiplied by “50” (250/5) to give the mass of bitumen in the oil sands.

Finally, a material balance was performed to obtain the composition of each component (solid, bitumen, and water) in the oil sands.

2.3 Recovery of Bitumen from Oil Sands

Bitumen flotation test was performed in a Denver flotation cell (shown in Figure 2.2) at 35^{o}C using an industry process water of pH 7.7 from Syncrude Canada Ltd. The pH of the pulp was adjusted to 8.5 by a pH modifier before each flotation test. For each test, 300 g of oil sands ore was processed in 950 mL of process water. The slurry containing the oil sands ore and process water was conditioned for 5 minutes at an agitation speed of 1500 rpm to enable the liberation of bitumen from the sand grains. Subsequently, air at 150 mL/min was introduced into the slurry and the bitumen froth was collected into four different thimbles of known masses at 3, 5, 10 and 20 minute time intervals after an initial 5 minute of conditioning. The composition (bitumen, solids and water) of the obtained bitumen froth was determined using the Dean-Stark apparatus with toluene as the solvent. The cumulative amount of bitumen recovered at each time intervals was calculated based on the bitumen content of the ores.

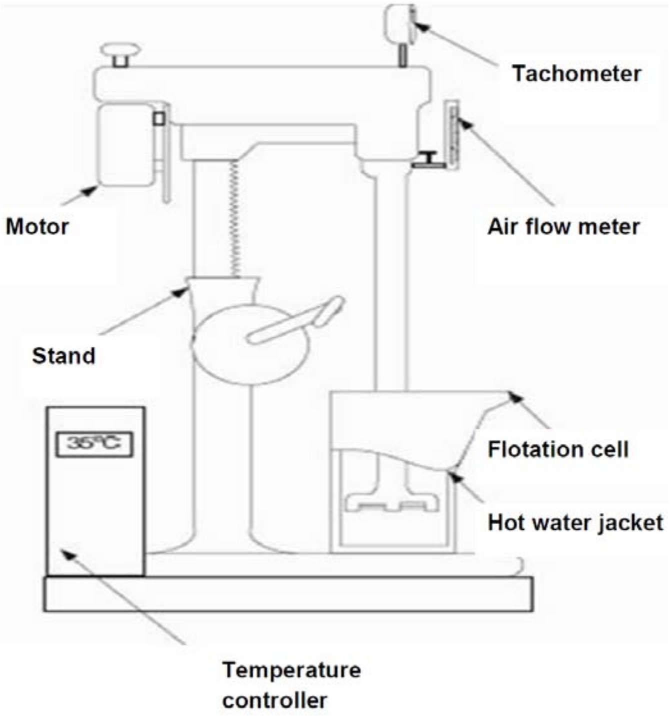

Figure 2.2: Schematic Diagram of a Denver Flotation Machine

2.4 Water Chemistry of Ores

The Syncrude Research Center[1] Canada's procedure for estimating the formation water chemistry of oil sands was used in this study. Approximately 50 mL of boiling deionized water was poured into a 250 ml beaker containing 50 g of oil sands. The mixture was stirred for 5 minutes and the bitumen froth skimmed off. The coarse sand grains were allowed to settle before filtration was performed to separate the aqueous solution from the sand grains and bitumen. The filtrate was sent to Maxxam Analytics to determine the pH, cation and anion contents of the connate water for each oil sands ore. The quantity of ions is presented as mg per litre of the water added to leach them from the oil sands.

2.5 Isolation of Solids

To extract solids, 300 g of ore was placed in a Denver flotation cell and agitated at 1,500 rpm in 950 mL of warm deionised water at 35^{o}C for 5 minutes to liberate bitumen from the oil sands (conditioning). Air at 150 mL/min was then introduced into the slurry to enable the liberated bitumen to be lifted to the surface of the slurry. The bitumen froth was skimmed off from the surface of the slurry and collected in a jar. This process continued for 20 minutes after which 250 mL of HepTol (heptane:toluene at 2:1 volume ratio) was added to the remaining slurry in the Denver flotation cell (tailings) and agitated for 5 minutes. The agitated slurry was transferred into a beaker and eventually poured into a separating funnel to enable separation into organic and aqueous phases.

The separated organic phase slurry from the heptol – tailings mixture was centrifuged at 20,000 g for 20 minutes and the supernatant was removed by decantation. The solids that were formed at the bottom of the centrifuge tubes after the centrifugation process were washed and centrifuged with heptol solvent to remove residual bitumen. When the supernatant became clear – indicating complete removal of bitumen, the washed solids were dried under vacuum.

The aqueous phase from the separating funnel was wet-sieved into distinct size fractions and the <45 µm solids in the slurry were concentrated by centrifugation at 20,000 g. All the solids obtained were subsequently dried under vacuum.

The recovery of the solids from the bitumen froth proceeded with the addition of 250 mL of heptol solvent in the jar containing the bitumen froth. The mixture was agitated in a shaker for 22 h after which, the mixture produced an organic and aqueous layer. The solids within each layer were treated in the same manner as used for the tailings slurry described above.

Consequently, at the end of the entire process, there were a total of four different process streams from which solids were extracted. Figure 2.3 depicts the entire process.

2.6 Pre-treatment of Organic-wet Solids

The organic matter (OM) adsorbed on the isolated solids from the organic-wet fractions was removed using both low temperature ashing (LTA) and hydrogen peroxide (H_2O_2). The details of the treatment are presented below.

2.6.1 Low Temperature Ashing

A plasma asher (K1050X) made by Quorum Emitech of Kent, England, was used in this study. The LTA uses a radio frequency (RF) radiation to dissociate, ionise and excite oxygen molecules into chemically excited states which are used to remove OM from samples. The process is carried out at a low pressure of 0.6 mbar. The combustion products are removed by a vacuum system.

The isolated solid was placed in ceramic Petri – dishes and loaded into the LTA. After evacuating the reaction chamber, the process gas (oxygen) was introduced

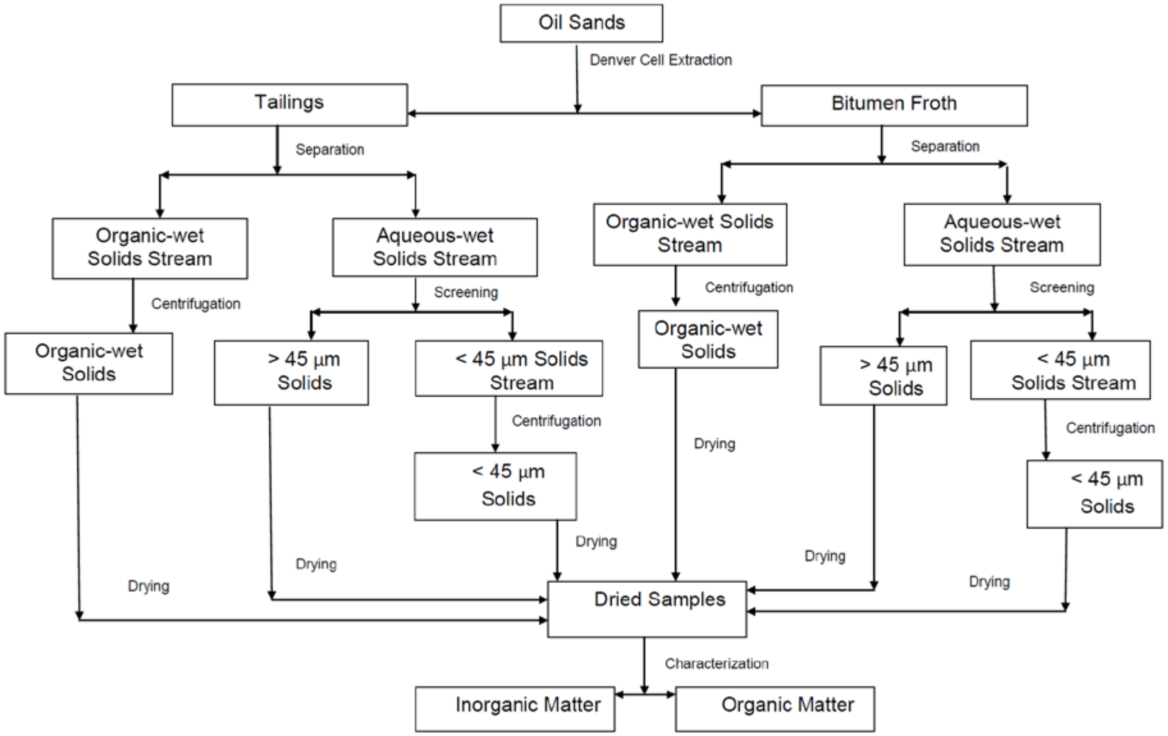

Figure 2.3: Description of the Isolation of Solids by Solvent –Water Extraction

into the LTA and an energizing RF power of 50 W was applied for 30 minutes. The samples were then stirred to move the isolated solid at the bottom to the top and vice versa, and reloaded back into the LTA for another 30-minute radiation. This process was repeated until the weight loss of the sample became negligible, which is an indication of the total OM removal from the samples by RF radiation.

2.6.2 Hydrogen Peroxide Treatment

Hydrogen peroxide (30% by weight) was obtained from Fisher Scientific and used as received. Approximately 25 mL of the H_2O_2 solution was added to a 700 mL beaker containing a given amount of isolated solids. Due to the hydrophobic nature of the isolated solids, those solids floated on the surface of the added H_2O_2 solution. When the beaker containing the slurry was placed in a heated water bath at a temperature between 60-70^{o}C, a violent reaction occurred and the slurry began to froth (a large beaker was used in this experiment to prevent sample loss due to frothing). Additional H_2O_2 solution was added continuously into the slurry as needed to avoid drying up the isolated solid. The reaction continued for about 4 h before the beaker was removed from the heated water bath. At this stage, 70 mL of de-ionized water was added to the slurry and the solids were separated from the H_2O_2 solution by a Millipore vacuum filter set. After filtration, about 100 mL of de-ionized water was used to wash off residual H_2O_2. The filter cake was dried in an oven at 105^{o}C for 24 h.

2.7 Characterization Techniques

The following characterization techniques were utilized in the course of this study.

2.7.1 Scanning Electron Microscope – Energy Dispersive X-ray Spectroscopy Analysis

The fine solids (<45 microns) isolated from oil sands as described above, were mounted on carbon shielded stubs and coated with carbon. They were analysed with a Hitachi S-2700 scanning electron microscope (SEM) equipped with a Princeton Gamma-Tech (PGT) IMIX digital imaging system and a PGT prism Intrinsic Germanium (IG) energy dispersive x-ray detector. The images were obtained at an accelerating voltage of 20 keV, working distance of 17 mm and magnifications of 700X and 3,000X. The elemental analysis is assumed to be semi-quantitative as the x-ray take off angle was not constant due to the roughness of the samples.

2.7.2 X-ray Diffraction

A Bruker D8 Advance x-ray diffractometer, equipped with an incident beam parabolic mirror, cobalt radiation (CoKα) and a linear detector (VANTEC-1^{TM}), was used to obtain the diffraction patterns of the clay (<2 µm) and silt (<45 µm) particles. The oriented clay slides and random powder clay samples were prepared for analysis.

Calcium-saturated oriented clay slides were prepared with the Millipore filtration method as described by Moore and Reynolds[2] to obtain the 00*l* diffraction pattern of the clays. This is to facilitate the identification of mixed layered clays present in the samples. In this method, a suspension of well dispersed clay-sized minerals (CSM) in deionised water was poured into a vacuum filter apparatus (Model, Millipore). After filtration with a 0.45 µm filter paper, 10 mL of 0.1 M calcium chloride solution was added to the formed filter cake to enable an exchange of Ca^{2+} ions in the interlayer of the clays. The filter cake was washed with deionised water to remove Cl^- ions and excess Ca^{2+} ions.

The clay cake formed on the filter paper was transferred onto a 25 mm quartz slide by placing the moist filter paper with clay onto it. After air-drying, the dry clay slides were placed in a desiccator containing a saturated magnesium nitrate solution to ensure that the clay samples were at high relative humidity (RH). The *00l* diffraction patterns at high RH were obtained from 5^0 (2ϴ) to 35^0 (2ϴ). The slides were then treated with ethylene glycol in a sealed desiccator placed in an oven at 65^oC for 24 h. The slides were then analyzed again after cooling at ambient temperature for at least an hour.

The procedure for quantitative analysis of oil sand clays from oriented slides using NEWMOD^{TM} and TOPAS^{TM} has been previously described by Kaminsky et al.[4]. Oriented, 1-dimensional diffraction patterns for glycolated, calcium-saturated pure clays were simulated using NEWMOD^{TM}. Subsequently, TOPAS^{TM} was used to obtain the peak positions and integrated intensities of the resulting simulated profiles. These parameters were used in quantifying the mixed layered and regular clays identified by the NEWMOD^{TM} derived model using the mineral intensity factor (MIF) as described by Moore and Reynolds[2]. The peak position and areas of the measured (experimental) diffraction patterns of the samples were likewise determined using TOPAS^{TM}. The clays that were considered for quantification include kaolinite (001), illite (002), kaolinte-smectite (001) and illite-smectite (002/003). In this study, illite (002) of the pure clay profile from NEWMOD^{TM} was used as the reference model clay.

$$\mathrm{MIF_i} = \mathrm{I_{p,i}} / \mathrm{I_{p,s}}$$

$$\text{Weight \% of i}^{\text{th}}\text{clay} = \frac{(\mathrm{I_i} / \mathrm{MIF_i})}{(\sum_{i=1}^{n} (\mathrm{I_i} / \mathrm{MIF_i}))} \mathrm{x100}$$

where $I_{p,i}$ and $I_{p,s}$ are the single peak intensity calculated using TOPAS^{TM} from NEWMOD^{TM} derived pure clay profiles of the ith modelled clay phase and a reference model clay phase (illite (002)), respectively. I_i is the peak area of the ith clay phase.

Sample preparation methods for XRD analysis of the random powder was described by Omotoso et al.[3]. Briefly, CSM were sieved onto a quartz sample holder to ensure that they were not lumped up together. While for the analysis of the silt, the samples were ground in 5 mL of methanol with a McCrone mill and agate balls placed in a 100 mL jar for 7 minutes. The purpose of grinding the samples was to reduce the particle size of the silt so that the bigger quartz particles would not overshadow the smaller minerals. To obtain a well dispersed powder sample, the ground silt went through a milling process by a Retsch MM301mixer mill in a 10 mL jar with plastic balls for 10 minutes. The resulting samples were sieved onto a quartz sample holder and levelled while trying to avoid preferential orientation of the samples. Diffraction patterns for the randomly oriented samples were obtained from 4^0 (2Θ) to 85^0 (2Θ).

The mineral phases in the random powder sample of clay-sized minerals (CSM) and silt was quantified with TOPAS^{TM}. The quantification was based on multiphase structure refinement (Rietveld) to give the weight percent of the minerals present. Model structures were taken from the Inorganic Crystal Structure Database (ICSD).

2.7.3 Fourier Transform Infrared Spectroscopy

A Biorad FTS 6000 was used to obtain infrared spectra of the CSM. The samples were mixed with KBr to 2 wt.% samples. The mixture was placed in a sample holder for absorbance measurement. The spectra were acquired at 4 cm^{-1} resolution over mid-infrared spectral region.

2.7.4 Elemental Analysis

A VarioMICRO elemental analyzer was used to obtain the elemental content of the samples. The sample weight used was between 2–5 mg and the combustion temperature was set at 1150°C. The combustion occurred in the presence of excess oxygen. The elements of interest include carbon (C), nitrogen (N), hydrogen (H) and sulphur (S).

2.7.5 Cation Exchange Capacity

Cation exchange capacity (CEC) was determined using both Methylene Blue (MB) and Copper Triethylenetetramine (CuTrien) methods. In the MB analysis, 0.2 g of samples were dispersed in 50 mL of 0.015M $NaHCO_3$ and 2 mL of 10 wt.% NaOH until a complete dispersion was attained using both a magnetic stirrer and sonicator. Before the MB titration, the pH of the slurry was adjusted to below 3 with 2 mL of 10 % vol/vol H_2SO_4. The titration was performed at 0.5 mL to 1 mL intervals with a fresh solution of 0.006 N Methylene Blue while the slurry was continuously stirred by a magnetic stirrer. In between each MB additions, a drop of the titrated mixture was placed on a Whatman qualitative filter paper to check for the presence of a light blue halo around the droplet. This halo indicates the end point of the MB titration. At the appearance of this halo, the slurry was left to stir for another two minutes to ensure that it is well mixed and homogenized. After which, another drop was taken from it and placed on the filter paper to check for the MB end point. This process was repeated until the blue halo was seen after the two minutes interval. The total volume of the MB added to the slurry to reach the end point was used to calculate the MB index according to the method of Hang and Brindley[5].

For CEC determination by CuTrien method, two portions of each sample (120 and 80 mg) were added to 30 mL deionized water in a beaker and dispersed in an ultrasonic bath for about 10 minutes, followed by the addition of 6 mL of Cu-trien prepared using the methodology of Meier and Kahr[6]. The mixture was shaken for an hour. The well mixed suspension was centrifuged at 15,000 g and the concentration of Cu (II) complex in the supernatant was determined using a UV-visible spectrophotometry. The difference between the UV absorption of the Cu-trien reagent and the absorption of the supernatant of a sample at 587 nm was used for the CEC calculation.

2.7.6 Surface Area

The specific surface area (SA) of the clay minerals was estimated from the results of XRD and methylene blue (MB) adsorption analysis. For SA analysis from XRD results, the methodology used by Nadeau[7], Omotoso et al.[8] and Kaminsky et al.[4] was adopted. This method uses the fundamental thickness of the clay particles, kaolinite, kaolinite-smectite, illite and illite-smectite to evaluate SA for each clay mineral. The total SA of the samples was determined from the quantitative XRD analysis. The MB adsorption method is based on the determination of cation exchange capacity (CEC) of clay minerals, as proposed by

Hang and Brindley[5]. The SA is related to the CEC through the following equation[5]:

$$\mathrm{SA}\ \left(\mathrm{m}^2/\mathrm{g}\right)=\mathrm{CEC}\ \left(\mathrm{from\ MB}\right)*130*0.0602$$

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CHAPTER THREE

PRE-TREATMENT METHODS OF SOLIDS FROM OIL SANDS[*]

3.1 Introduction

Oil sands in Alberta, Canada comprise of silica sand and other minerals impregnated with highly viscous bitumen. Its deposits are located in the Athabasca, Cold Lake and Peace River regions[1] of Northern Alberta. Bitumen is produced from oil sands by either in-situ techniques or by hot water-based extraction of surface – mined oil sands. The main challenge posed by the water based process is the management of the large quantities of water required for bitumen extraction. Over 70% of the water is re-used but the remaining 30% is trapped in slow-settling tailings ponds[2] containing mostly clay-sized minerals (CSM). An understanding of the CSMs is therefore critical not only to extraction of bitumen and bitumen froth cleaning, but also to the development of better tailings reclamation technologies.

Characterization of solids to determine particle size distribution, mineral phases, specific surface areas, and cation exchange capacity is essential to the success of the oil sands industry. A common prerequisite for effective characterization is to remove organic matter (OM) from these solids without changing their inorganic phases. The presence of a significant amount of OM can inhibit the dispersion of

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[*] This chapter is based on: Adegoroye, A; Uhlik, P.; Omotoso, O.; Xu, Z.; Masliyah, J. *Energy and Fuels.* **2009**, *23,* pp 3716 – 3720.

CSM in slurry and lead to broad diffraction peaks and increased background noise that may interfere with quantitative analysis of x-ray diffraction (XRD) peaks[3]. Chemical treatments are often used to remove OM from CSM surfaces prior to their characterization. The oxidizing agents[3,4] that are commonly used in chemical treatments are hydrogen peroxide, sodium hypobromite, disodium peroxodisulfate and sodium hypochlorite, which is present in most commercially available bleach. Treatment of CSM with these chemicals may change the structure[3] of the CSM and hence lead to false identification of altered mineral phases.

Another technique that has been explored in the removal of OM in soil and samples containing predominantly OM such as coal is *Low Temperature Ashing (LTA)*. This technique uses radio frequency radiation to excite a gas – frequently oxygen, to remove OM from a sample at a temperature below 100°C. According to Marcoen (1975) and Sullivan et al. (1987), LTA removes OM from the mineral matrix of soil with minimal disturbance and damage to its inorganic constituent[5-9] because of its low operating temperature. This attribute makes LTA a better technique for the removal of OM from CSM isolated from heavy oil processing. LTA could avoid possible change in the structure of CSM while effectively removing organic matter. LTA has been employed by Smith et al (1974). in the study of oil shales[7,10], Soong et al. (1977) on coals[7,11], Gleit et al. (1962) for biological materials[7,12], De Kimpe et al.(1990) on humic and fulvic acid[5,7], Sullivan et al. (1987) in sample preparations for microscopy[5,8] and D'Acqui et al.(1999) on tropical crusting soil[5]. In this study, LTA is exploited to remove OM from CSM extracted from oil sands for characterization of mineral phases consisting of CSM.

The objective of this study is to *(1)* explore and compare the effectiveness of H_2O_2 and LTA treatment for the removal of OM from CSM isolated from oil sands; *(2)* study the effect of OM removal by the two methods on CSM structure, cation exchange capacity (CEC) and wettability, and *(3)* compare the extent of OM removal from CSM isolated from the tailings and bitumen froth obtained using warm water extraction in a Denver flotation cell. The best technique would prove useful for CSM characterization in the future as applied to the oil sands industry.

3.2 Experimental Section

3.2.1 Clay-sized Minerals

Weathered oil sands ore of estuarine origin obtained from Syncrude Canada Ltd. containing 12% bitumen, 87% solids and 1% water was used in this study. To extract CSM, 300 g of this ore was placed in a Denver flotation cell and agitated at 1,500 rpm in 950 mL of warm deionised water at $35^{o}C$ for 5 minutes to liberate bitumen from the oil sands (conditioning). Air at 150 mL/min was then introduced into the slurry to enable the liberated bitumen to be lifted to the surface of the vessel. The bitumen froth was skimmed off the surface of the slurry and collected in a jar. This process was done for 20 minutes after which 250 mL of HepTol (heptane:toluene at 2:1 volume ratio) was added to the remaining slurry of the Denver flotation cell (tailings) and agitated for 5 minutes. The agitated slurry was transferred into a beaker and eventually poured into a separating funnel to enable separation into organic and aqueous phases.

The separated organic phase slurry from the heptol – tailings mixture was centrifuged at 20,000 g for 20 minutes and the supernatant was removed by decantation. The solids that were formed at the bottom of the centrifuge tubes after the centrifugation process were washed and centrifuged with heptol solvent to remove residual bitumen. When the supernatant became clear – indicating complete removal of bitumen, the washed solids were dried under vacuum.

The aqueous phase from the separating funnel was wet-sieved into distinct size fractions and the <45 µm solids in the slurry were concentrated by centrifugation at 20,000 g. All the solids obtained were subsequently dried under vacuum.

The recovery of the solids from the bitumen froth proceeded with the addition of 250 mL of heptol solvent in the jar containing the bitumen froth. The mixture was agitated in a shaker for 22 h after which, the mixture produced an organic and aqueous layer. The solids within each layer were treated in the same manner as used for the tailings slurry described above.

The isolated solids from the organic phase (bitumen froth and tailings) are of interest in this study. In order to accurately characterize the isolated solids the OM has to be removed. The CSM in the isolated solids were separated from silt by sedimentation. The CSM from the tailings and bitumen froth were split into three fractions – A, B, and C. Fraction A was left untreated, while fractions B and C were treated with LTA and H_2O_2, respectively. The samples from the tailings were labeled as TA, TB and TC, while those from the bitumen froth were FA, FB and FC. For control measures, XRD and CEC analysis were performed on an untreated (DV) and LTA – treated (DVA) model clays containing predominantly illite – smectite and quartz.

3.2.2 Low Temperature Ashing

A plasma asher (K1050X) made by Quorum Emitech of Kent, England, was used in this study. It is a barrel reactor type, identical[5, 13] to the type used by Favia (1996) and D'Acqui (1999). The LTA uses a radio frequency (RF) radiation to dissociate, ionise and excite oxygen molecules into chemically excited atoms[14] which are used to remove OM from samples. The process is carried out at a low pressure of 0.6 mbar. The combustion products are removed by a vacuum system.

CSM was placed in ceramic Petri – dishes and loaded into the LTA. After evacuating the reaction chamber, the process gas (oxygen) was introduced into the LTA and an energizing RF power of 50 W was applied for 30 minutes. The samples were then stirred to move the CSM at the bottom to the top and vice versa, and reloaded back into the LTA for another 30-minute radiation. This was repeated until the weight loss of the sample became negligible, which is an indication of the total OM removal from the samples.

3.2.3 Hydrogen Peroxide Treatment

Hydrogen peroxide (30% by weight) was obtained from Fisher Scientific and used as received. Approximately 25 mL of the H_2O_2 solution was added to a 700 mL beaker containing a given amount of CSM. Due to the hydrophobic nature of the CSM, they floated on the surface of the added H_2O_2 solution. When the beaker containing the slurry was placed in a heated water bath at a temperature between 60 – 70^{o}C, a violent reaction occurred and the slurry began to froth (a large beaker was used in this experiment to prevent sample loss due to frothing). Additional H_2O_2 solution was added continuously into the slurry as needed to avoid drying up the CSM. The reaction continued for about 4 h before the beaker was removed from the heated water bath. 70 mL of de-ionized water was added to the slurry and the solids were separated from the H_2O_2 solution by a Millipore vacuum filter set. After filtration, about 100 mL of de-ionized water was used to wash off residual H_2O_2. The filter cake was dried in an oven at 105^{o}C for 24 h.

3.2.4 Fourier Transform Infrared Analysis

A Biorad FTS 6000 was used to obtain infrared spectra of the CSM. The samples were mixed with KBr to 2 wt.% samples. The mixture was placed in a sample holder for absorbance measurement. The spectra were acquired at 4 cm^{-1} resolution over mid-infrared spectral region.

3.2.5 X-ray Diffraction Analysis

Diffraction patterns were collected on a Bruker D8 Advance (vendor, Bruker AXS) with cobalt radiation (CoKα) and an incident beam parabolic mirror. A VANTEC-1^{TM} linear detector and a quartz sample holder were used.

3.2.6 Elemental Analysis

The elemental content of the CSM before and after LTA and H_2O_2 treatment was determined with a VarioMICRO elemental analyzer. The combustion temperature was set at 1150^{o}C and the sample weight used was between 2–5 mg. The elements of interest include carbon (C), nitrogen (N) and hydrogen (H).

3.2.7 Cation Exchange Capacity

Cation exchange capacity (CEC) was determined using both Methylene Blue (MB) and Copper Triethylenetetramine (CuTrien) methods for the treated samples containing some silt (<45 µm), an untreated (DV) and LTA treated (DVA) model clays containing predominantly illite – smectite and quartz.

In the MB analysis, 0.2 g of samples were dispersed in 50 ml of 0.015M $NaHCO_3$ and 2 mL of 10% w/w NaOH until complete dispersion was attained using both a magnetic stirrer and sonicator. The pH of the slurry was adjusted with 2 mL of 10% vol/vol H_2SO_4 to a pH below 3, before the MB titration commenced. The titration was performed at 0.5 mL to 1 mL intervals with a fresh solution of 0.006N Methylene Blue while the slurry was continuously stirred on a magnetic stirrer. In between each MB additions, a drop of the titrated mixture was placed on a Whatman qualitative filter paper to check for the presence of a light blue halo around the droplet. This halo indicates the end point of the MB titration. At the appearance of this halo, the slurry was left to stir for another two minutes to ensure that it is well mixed and homogenized. After which, another drop was taken from it and placed on the filter paper to check for the MB end point. This process continued until the blue halo was seen after the two minutes interval. The total volume of the MB added to the slurry to reach the end point was used to calculate the MB index according to the method of Hang and Brindley[15] (1970).

For CEC determination by CuTrien method, two portions of each sample (120 and 80 mg) were added to 30 mL deionized water and dispersed in an ultrasonic bath for about 10 minutes, followed by the addition of 6 mL of Cu-trien prepared using the methodology of Meier and Kahr[16] (1999). The mixture was shaken for an hour. The well mixed suspension was centrifuged at 15,000 g and the concentration of Cu (II) complex in the supernatant was determined using a UV – visible spectrophotometry (model, Varian). The difference between the UV absorption of the Cu-trien reagent and the absorption of the supernatant of a sample at 587 nm was used for the CEC calculation.

3.2.8 Wettability Test

The wettability of CSM was measured with a Drop Shape Analyzer (DSA10, Kruss). The CSM cake was prepared on a filter paper after filtration with a

Millipore vacuum filter set. Approximately 15 µL of water was placed on the surface of the CSM cake with a syringe. The shape of the water drop was recorded and the profile of the drop shape was analyzed using vendor – provided imaging analysis software to obtain the contact angle values.

3.3 Results and Discussion

3.3.1 Infrared Spectra

Figures 3.1 and 3.2 show the infrared spectra of solid samples extracted from the tailings and bitumen froth, respectively. It can be noted that the untreated CSM (TA and FA) exhibit the characteristic $–CH_2–$ and $–CH_3$ vibration bands at 2926 cm^{-1} and 2854 cm^{-1}, respectively. The absence of these bands after treatment of the CSM by LTA and H_2O_2 indicates the effective removal of OM by these two methods.

A broad band between 1438 – 1500 cm^{-1} and a sharp band at 864 cm^{-1} were noted in the spectra of the untreated and LTA treated CSM. These bands, the most intense bands for siderite[17-22] ($FeCO_3$), were absent in the H_2O_2 treated CSM. The absence of these bands for H_2O_2 treated CSM indicates the conversion of siderite, possibly by oxidation of iron and departure of CO_2. Clearly caution has to be excised when removing OM by oxidizing reagent such as H_2O_2.

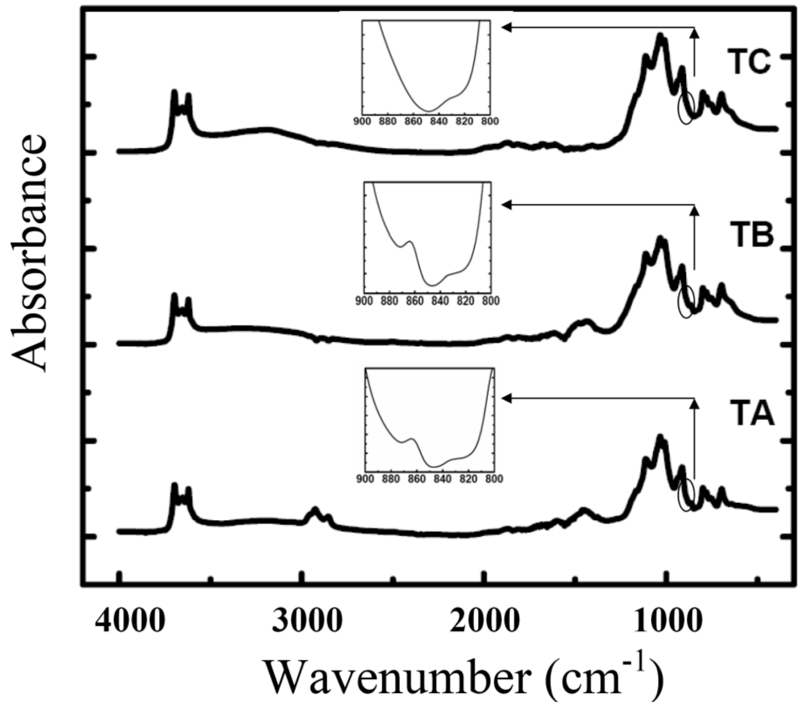

Figure 3.1: Infrared Spectra of Untreated (TA), LTA and H_2O_2 Treated (TB and TC, Respectively) CSM from the Tailings

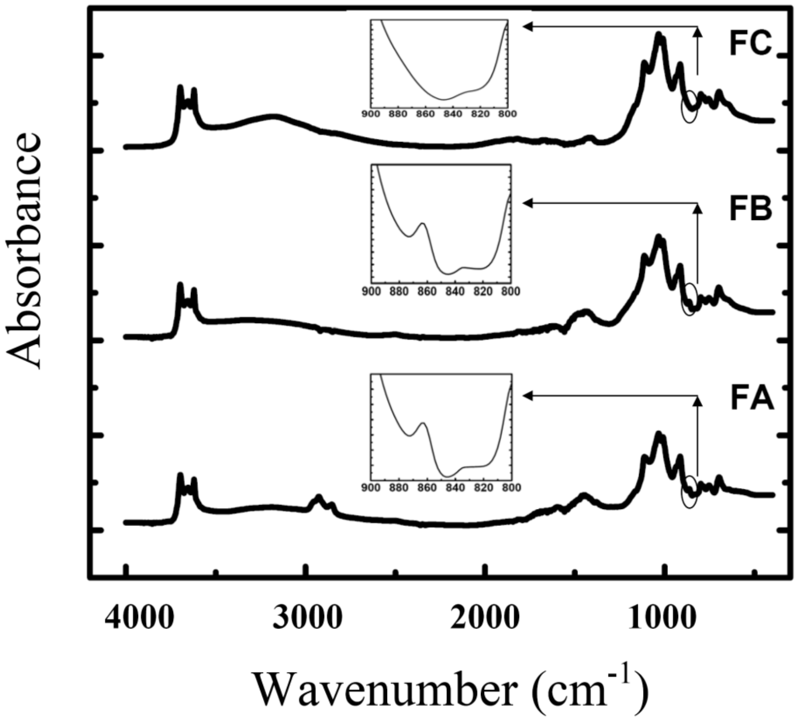

Figure. 3.2: Infrared Spectra of Untreated (FA), LTA and H_2O_2 Treated (FB and FC, Respectively) CSM from the Bitumen Froth

3.3.2 X-ray Diffraction Pattern

The x-ray diffraction patterns in Figures 3.3 and 3.4 show the presence of illite, kaolinite, and quartz in all the samples. The peaks labeled as “C” are bayerite contaminants from the weighing dish used in drying the samples. Presence of siderite indicated as “S” at 37.2^o is evident in the untreated (TA and FA) and LTA treated samples TB and FB. This peak is absent in the H_2O_2 treated CSM (TC and FC). This observation confirms the oxidation of siderite ($FeCO_3$) by H_2O_2, as inferred from the infrared spectra. It is also interesting to note that the relative intensity of the siderite diffraction peak is much stronger in the froth CSM than in the tailings CSM, indicating an enrichment of siderite in bitumen froth.

To ensure that LTA does not alter the mineralogy of CSM, the diffraction patterns of an untreated (DV) and LTA – treated model clays (DVA) were obtained as shown in Figure 3.5. It can be observed that the model clays contains illite and quartz which were not changed after undergoing the LTA treatment.

3.3.3 Elemental Composition

The results of the elemental analysis are given in Table 3.1. In general, the CSM from bitumen froth contained slightly higher amount of carbon than those from the tailings. Both H_2O_2 and LTA treatments reduced significantly the amount of carbon on the CSM. The H_2O_2 treated CSM (TC and FC) were found to have the least percentage of carbon while the LTA treated CSM (TB and FB) were found to contain the least amount of hydrogen albeit a little more carbon than the H_2O_2

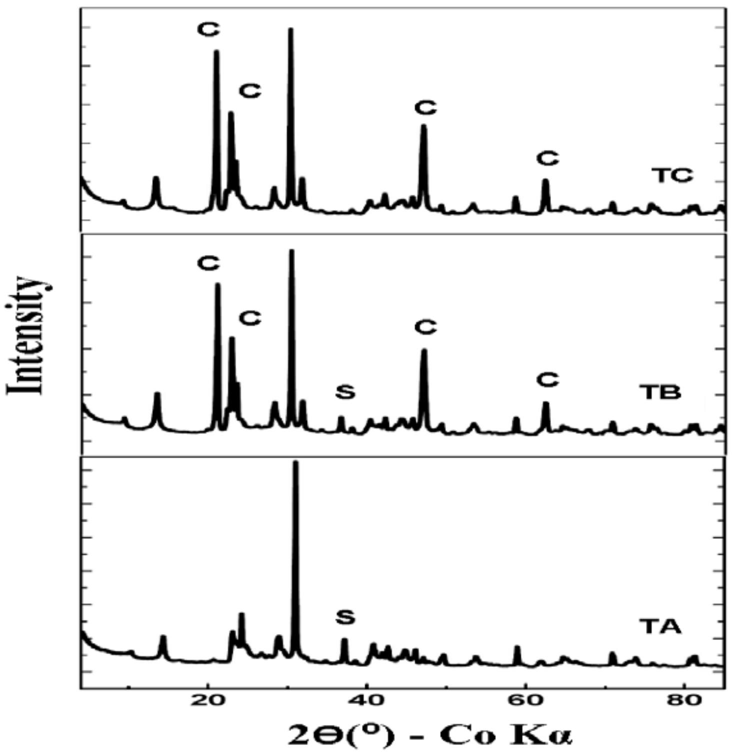

Figure 3.3: X-ray Diffraction Patterns of Untreated (TA), LTA and H_2O_2 Treated CSM from Tailings (TB and TC)

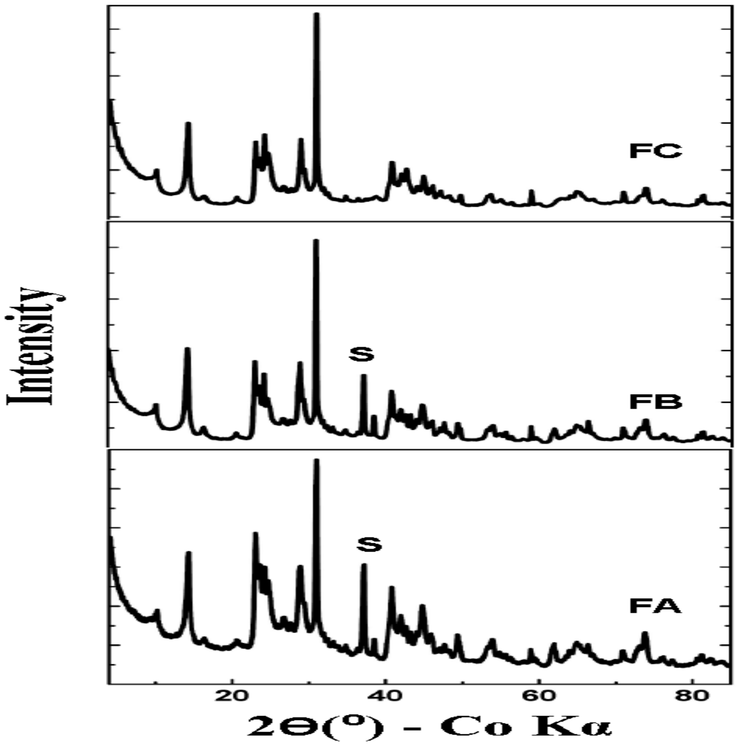

Figure 3.4: X-ray Diffraction Patterns of Untreated (FA), LTA and H_2O_2 Treated CSM from the Bitumen Froth (FB and FC)

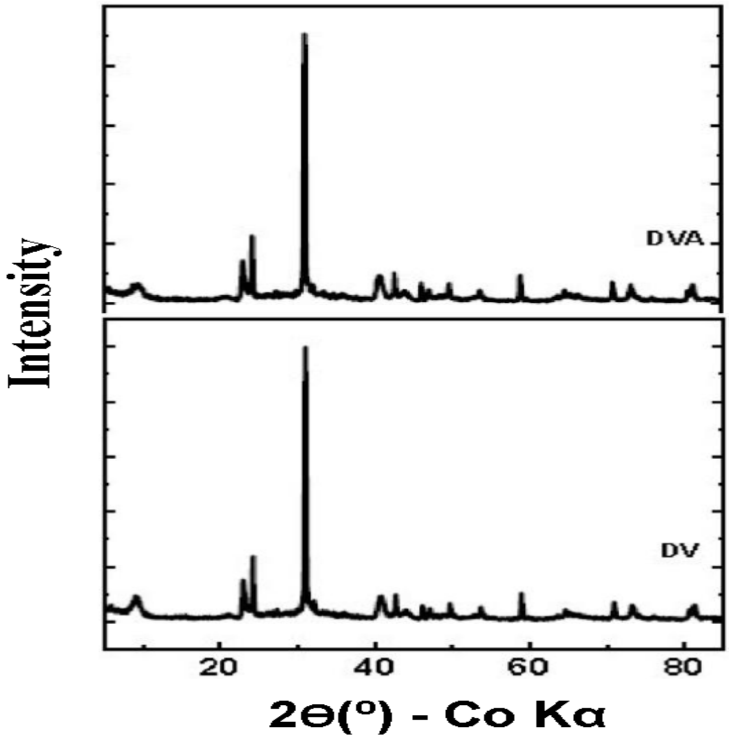

Figure 3.5: X-ray Diffraction Patterns of Untreated and LTA Treated Model Clays (DV and DVA)

Table 3.1: Elemental Composition of Samples

Sample	**Element (% wt/wt)**		
	Carbon	**Hydrogen**	**Nitrogen**
Untreated TA	13.11	2.07	0.36
LTA Treated TB	2.09	1.05	0.13
H_2O_2 Treated TC	0.39	1.31	0.19
Untreated FA	17.01	2.28	0.42
LTA Treated FB	5.01	1.28	0.18
H_2O_2 Treated FC	0.52	1.47	0.30

treated CSM. The presence of slightly higher carbon content in the LTA treated CSM may be attributed to the conversion of siderite ($FeCO_3$) to carbon dioxide and iron oxides during the analysis at 1150°C.

3.3.4 Cation Exchange Capacity

The results in Table 3.2 show similar CEC values determined by CuTrien and MB methods for LTA treated samples. However, the CEC values determined by CuTrien method are significantly higher than that determined using MB method for H_2O_2 treated samples. This finding indicates that the presence of iron oxides produced by H_2O_2 treatment has an effect on CuTrien analysis.

To confirm that the LTA treatment does not change the CEC of clays, model clay containing predominantly illite – smectite and quartz (DV) were treated by LTA and CEC was determined. The results in Table 3.2 clearly show identical CEC values for LTA – treated (DVA) and untreated model clays (DV), confirming that the LTA treatment has a negligible effect on CEC.

3.3.5 Wettability Test Result

The water contact angles on the pellets of untreated CSM from tailings and bitumen froth were determined to be 90.6° and 93.8°, respectively. In an attempt to measure contact angle of water on the treated CSM, water drop disappeared quickly, indicating that these samples are extremely hydrophilic. Clearly the removal of hydrocarbons from CSM surfaces by H_2O_2 or LTA treatment made the original hydrophobic solids hydrophilic.

Table 3.2: Effect of LTA and H_2O_2 Treatment on Cation Exchange Capacity

Sample	**Methylene Blue (meq/100 g)**	**CuTrien (meq/100 g)**
Model Clay - DV (<32 μm)	30	32
Ashed Model Clay -DVA (<32 μm)	31	30
TB (<45 μm)	10	8
TC (<45 μm)	10	17
FB (<45 μm)	14	12
FC (<45 μm)	13	21

3.4 Summary

Removal of OM by either LTA or H_2O_2 is effective as indicated by the results of infrared spectra, x- ray diffraction and elemental analysis, and wettability tests. Upon H_2O_2 or LTA treatment, the IR bands at 2926cm^{-1} and 2854 cm^{-1} corresponding to $–CH_2–$ and $–CH_3$ stretching vibrations disappeared, indicating the removal of OM. Accompanied with the departure of OM, the amount of carbon, hydrogen and nitrogen on the treated CSM were reduced significantly, making the treated particles hydrophilic.

Compared with H_2O_2 treatment, removal of OM by LTA is preferred as it does not change the mineral phases of inorganic matter. In the case of H_2O_2 treatment, siderite was found to be oxidized as indicated by the results of infrared spectra, XRD and CEC analysis. My study clearly shows that LTA is a better choice in OM removal from CSM isolated from oil sands and its usage would guarantee more accurate characterization of original mineral solids phases than the widely used H_2O_2 treatment.

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CHAPTER FOUR

CHARACTERIZATION OF ORGANIC COATED SOLIDS ISOLATED FROM DIFFERENT OIL SANDS ORES[*]

4.1 Introduction

Organic matter (OM) coated on solids in oil sands has long been recognized to have a detrimental effect on bitumen separation from oil sands and upgrading to synthetic crude oil. Previous studies showed that OM, which is insoluble in common organic solvents, such as toluene and isopropyl alcohol, is often associated with fines fraction (<45 µm) of particulate minerals present in oil sands[1-3]. This makes the solid surface hydrophobic[4], permitting particle bridging by the adsorption of residual bitumen. The presence of these *hydrophobic* solids has been linked to poor bitumen froth quality, fouling of bitumen upgrading equipment and poor compaction of the fine grained sludge in tailings slurry[4-11]. Hence, a better understanding of the organo-mineral interaction would be beneficial to the oil sands industry.

Adsorption of OM on clay minerals involves the accumulation of organic molecules or ions from a gaseous or liquid phase onto the surface of clay mineral particles[12]. According to Jacks[13, 14] clay-organic complexes can be referred to as the union of inorganic mineral and organic matter to form an organo-mineral complex. Their association involves different degrees of interactions from loosely

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bound organic and mineral particles to tightly bound complexes[15]. Physiochemical interactions are the essence at the molecular scale and could be through such mechanisms from electrostatic and van der Waals forces to specific coordination bonds and hydrogen bonds[15]. The kind of bond and the surface areas engaged in the contact determine the adhesion of organo-mineral association[15].

Repulsion usually occurs between organic anions and negatively charged clay surfaces[13]; hence, polyvalent cations are required to form a bridge between these two entities. These cations neutralize the charge on the clay and the acidic functional group of the OM such as COO^-. The importance of polyvalent cations in the context of OM binding with fine clays is well documented in literature[13,16,17]. These cations are usually Ca^{2+}, Fe^{3+} and Al^{3+}. Greenland[18] observed that OM bound with Ca^{2+} could be easily displaced by a monovalent cation[13]. This is due to the fact that Ca^{2+} does not form strong coordination complexes with OM and would be effective only to the extent that a bridge linkage could be formed[13]. Unlike Ca^{2+}, the displacement of Fe^{3+} and Al^{3+} would be difficult and may require a strong chelating agent as they form strong bonds with OM[13].

Another mechanism of OM adsorption is by the formation of strong coordination bond (ligand exchange) and simple anion exchange with hydrous oxides of iron and aluminium[13]. The presence of these hydrous oxides on clay minerals dominates surface reactions and induces a cementation effect that leads to the development of strong aggregation, formation of concretion and crust[13,19,20].

Anion exchange[13] is possible because of the presence of positive sites on these hydrous oxides at pH below 8. However, the exchanged organic anions could be disengaged at a higher pH or by leaching with NaCl or NH_4Cl[13]. The coordination bond or ligand exchange takes place when the anionic group penetrates the coordination shell of aluminium or iron and becomes incorporated by displacing the surface hydroxyl layer[13,18]. OM may interact with crystalline oxides in this manner[13].

Furthermore, according to Carter et al.[21], aspartic acid-enriched OM may be preferentially adsorbed on carbonate surfaces as opposed to non-carbonate surfaces. This was also observed by Chave[21, 22] and Suess[21, 23, 24], - who illustrated the specific adsorption of surface-active OM from sea water on carbonated grains. Their association could be due to the similarity between carbonate anions and carboxyl groups[21].

In a previous study of a low grade-high fines oil sands ore using solvent–extraction technique, Kotlyar et al.[6] suggested that residual organic matter may be bound to metal oxides and hydrous oxides. It was also observed that siderite could be a major inorganic component in the organic-mineral complexation[6]. In this study, organic coated solids are extracted from different oil sands ores –

weathered, high- and low-fines; using a warm – water based extraction process with a Denver flotation cell. The partitioning of the organic coated solids and its constituents in the bitumen froth and tailings is studied. The interactions of OM with minerals and their effect on oil sands processability from the different oil sand ores are also investigated.

4.2 Experimental Section

4.2.1 Organic Coated Solids

Three different oil sand ores with varying degrees of weathering were studied. For control measures, they were compared with both a low and high fines oil sand ore. The weathered ores coded as “W1” and “W2” were from Suncor Energy Inc. and “W3” from Syncrude Canada Ltd., while the low fines ore “G” was from Suncor Energy Inc. and high fines ore “P” from Syncrude Canada Ltd. The procedure used for extracting the solids from the different oil sand ores has been described in a previous communication[25] and is described briefly below.

To isolate the solids, 300 g of ore was placed in a Denver flotation cell and agitated at 1,500 rpm in 950 mL of warm deionised water at 35°C for 5 minutes to liberate bitumen from the oil sands (conditioning). Air at 150 mL/min was then introduced into the slurry to enable the liberated bitumen to be lifted to the surface of the slurry. The bitumen froth formed on the top of the slurry was skimmed off and collected in a jar. This process continued for 20 minutes after which 250 mL of heptol (heptane:toluene at 2:1 volume ratio) was added to the remaining tailings in the Denver flotation cell and agitated for 5 minutes. The agitated slurry was transferred into a beaker and eventually poured into a separating funnel to enable partitioning of its constituents into organic and aqueous phases.

The separated organic phase slurry from the heptol – tailings mixture was centrifuged at 20,000 g for 20 minutes and the supernatant was removed by decantation. The solids that were formed at the bottom of the centrifuge tubes after the centrifugation process were washed and centrifuged with heptol solvent to remove residual bitumen. When the supernatant became clear – indicating complete removal of bitumen, the washed solids were dried under vacuum.

The aqueous phase from the separating funnel was wet-sieved into distinct size fractions and the <45 µm solids in the slurry were concentrated by centrifugation at 20,000 g. All the solids obtained were subsequently dried under vacuum.

The recovery of the solids from the bitumen froth proceeded with the addition of 250 mL of heptol solvent in the jar containing the bitumen froth. The mixture was agitated in a shaker for 22 h after which, the mixture produced an organic and aqueous layer. The solids within each layer were treated in the same manner as used for the tailings slurry described above.

The solids partitioned in the organic phase from bitumen froth and tailings are of interest in this study. The amount of these solids and some other oil sands properties are presented in Table 4.1. The solids partitioned in the organic phase from the bitumen froth of the weathered (W1, W2 and W3), low (G) and high (P) fines oil sands ores are labeled as W1OF, W2OF, W3OF, GOF and POF, respectively, and those from the tailings as W1OT, W2OT, W3OT, GOT and POT. For the XRD analysis, the samples were separated into clay (<2 µm) and silt fractions (2-60 µm) by centrifugation at 1280 g for 4 minutes after the removal of OM. Letters "C" and "S" were placed in front of the sample labels to indicate their fractions – clay and silt. For instance, CGOF refers to clay samples from the bitumen froth of the low fines ore.

4.2.2 X-ray Diffraction Analysis

A Bruker D8 Advance equipped with an incident beam parabolic mirror for cobalt radiation (CoKα) and a linear detector (VANTEC-1^{TM}) was used to obtain the diffraction patterns of the clay and silt portions of the samples. The samples were placed on a 25 mm (diameter) quartz sample holder.

Quantification of the mineral phases present in the random powder sample of clay sized – minerals (CSM) and silt was obtained with TOPAS^{TM}. This is based on multiphase structure refinement (Rietveld) to give the weight percent of the minerals present. Model structures were taken from the Inorganic Crystal Structure Database (ICSD).

4.2.3 Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy

Powder samples were mounted on carbon shielded stubs and coated with carbon. They were analyzed with a Hitachi S-2700 scanning electron microscope (SEM) equipped with a Princeton Gamma-Tech (PGT) IMIX digital imaging system and a PGT prism Intrinsic Germanium (IG) energy dispersive x–ray spectroscopy (EDX) analysis detector. The elemental analysis by EDX is semi–quantitative as the x–ray take off angle was not constant due to the roughness of the samples.

4.2.4 Elemental Analysis

A VarioMICRO elemental analyzer was used to obtain the elemental content of the samples. The sample weight used was between 2–5 mg and the combustion temperature was set at 1150^{o}C. The combustion occurred in the presence of excess oxygen. The elements of interest include carbon (C), nitrogen (N), hydrogen (H) and sulphur (S).

4.2.5 Fourier Transform Infrared Analysis

Infrared spectra of the samples were obtained with a Biorad FTS 6000. Samples were mixed with KBr to 2 wt.% of the sample. The mixture was placed in a sample holder for diffuse reflectance IR Fourier transform spectroscopy (DRIFTS) analysis.The spectra were acquired at 4 cm^{-1} resolution over mid-infrared spectral region. The results are presented in Kubelka – Munk unit.

4.2.6 Bitumen Flotation Kinetics

Bitumen flotation test was conducted in a Denver flotation cell at 35°C using an industry process water of pH 7.7 from Syncrude Canada Ltd. The pH of the pulp was adjusted to 8.5 by a pH modifier before each flotation test. For each test, 300 g of oil sands ore was processed in 950 mL of process water. The slurry containing the oil sands ore and process water was conditioned for 5 minutes at an agitation speed of 1500 rpm to enable the liberation of bitumen from the sand grains. Subsequently, air at 150 mL/min was introduced into the slurry and the bitumen froth was collected into four different thimbles of known masses at 3, 5, 10 and 20 minute time intervals after the initial 5 minutes of conditioning. The composition (bitumen, solids and water) of the obtained bitumen froth was determined using the Dean-Stark apparatus with toluene as the solvent. The cumulative amount of bitumen recovered at each time intervals were calculated based on the bitumen content of the ores.

4.3 Results and Discussion

4.3.1 Oil Sands Properties

The properties of the ores used and the percent amount of solids extracted in organic phase from bitumen froth and tailings are given in Table 4.1. The values are within an error of ±0.3 by standard deviation. The weathered ores contain the largest amount of solids extracted (bitumen froth and tailings – combined) into the organic phase and the low fines ore contains the least. The solids extracted into

Table 4.1: Properties of Oil Sand Ores

Oil Sands Ore	**Composition (%)**						**Formation Water Chemistry**			
	Bitumen	**Water**	**Total Solids (including fines)**	**Fines in Oil Sands (<45 µm)**	**Oil –Wet Solids in Bitumen Froth (<60 µm)**	**Oil-Wet Solids in Tailings (<60 µm)**	**pH**	**Calcium (Ca) (mg/L)**	**Magnesium (Mg) (mg/L)**	**Hardness ($CaCO_3$) (mg/L)**
W1	14.5	1.0	84.5	8.77	0.96	7.97	6.4	6.5	4.5	35
W2	12.2	2.6	85.2	5.94	0.77	2.83	5.6	6.8	5.7	41
W3	12.0	1.0	87.0	4.14	1.41	3.59	5.1	75.0	16.0	250
P	9.6	3.4	87.0	18.00	1.04	1.48	8.0	2.9	2.1	16
G	15.9	1.5	82.6	2.60	0.54	0.39	6.7	0.9	3.6	17

organic phase are considered hydrophobic. The formation water of weathered ores has the lowest pH (<7) which is often indicative of mineral (especially pyrite) oxidation. The low pH causes calcite dissolution and a corresponding increase in Ca concentrations in the formation water. In addition to the degree of oxidation and pH, the concentration of Ca in solution also depends on the amount of calcium-bearing minerals in the ores. W3 of the lowest formation water pH appears to be the most oxidized, leading to a much higher concentration of Ca in the formation water. Interestingly, this ore also contains the highest amount of pyrite (Tables 4.2 and 4.3), a precursor for oxidation. High content of organic-coated solids, mineral (or bitumen) oxidation, high concentration of divalent cations in formation water and high fines content are all deleterious to bitumen extraction.

4.3.2 Mineral Composition

Figures 4.1 and 4.2 depict the x-ray diffraction patterns of solids in clay fractions isolated into the organic phase from the bitumen froth and tailings, respectively. The presence of illite, kaolinite, k-feldspar and quartz are evident in this fraction. The results of the quantitative mineral phase analysis by TOPAS^{TM} for the clay and silt fractions are given in Tables 4.2 and 4.3, respectively. It is interesting to note that the isolated solids from the weathered (W1, W2 and W3) and high fines (P) ores contain both siderite ($FeCO_3$) and pyrite (FeS_2) which are absent in the low fines ore (G). These minerals are more distinctive in W3, when compared with the other ores. The presence of calcite ($CaCO_3$), albeit low, is observed in the

Table 4.2: Mineral Phases Present in the Clay Fraction of Isolated Solids

Mineral Phase	**Samples (wt.% Rietveld)**									
	CW1OF	**CW1OT**	**CW2OF**	**CW2OT**	**CW3OF**	**CW3OT**	**CPOF**	**CPOT**	**CGOF**	**CGOT**
Siderite	6	4	2	2	7	5	6	0	0	0
Kaolinite	53	48	52	49	54	48	29	28	19	20
Illite	20	22	25	18	19	10	37	33	11	31
Quartz	10	17	13	23	10	22	15	30	11	31
Zircon	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	0	< 0.5
Microcline	4	4	3	4	3	7	4	4	4	6
Rutile	1	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1	1	0	1
Albite calcian	3	3	1	2	2	4	2	3	2	3
Pyrite	1	< 0.5	1	1	3	1	1	< 0.5	0	0
Anatase	3	1	2	2	2	2	5	2	3	2
Calcite	0	0	0	0	0	0	0	0	3	< 0.5

Table 4.3: Mineral Phases Present in the Silt Fraction of Isolated Solids

Mineral Phase	**Samples (wt.% Rietveld)**									
	SW1OF	**SW1OT**	**SW2OF**	**SW2OT**	**SW3OF**	**SW3OT**	**SPOF**	**SPOT**	**SGOF**	**SGOT**
Siderite	11	1	1	0	10	8	14	2	0	0
Kaolinite	38	9	27	8	45	17	15	10	44	10
Mica	23	8	23	7	22	11	23	12	20	8
Quartz	16	76	36	77	12	55	27	68	23	74
Zircon	1	< 0.5	1	< 0.5	< 0.5	< 0.5	3	< 0.5	1	< 0.5
K-feldspar	4	3	4	4	1	3	4	4	5	4
Rutile	2	1	3	2	1	1	3	1	2	1
Plagioclase	2	1	2	1	< 0.5	< 0.5	4	2	2	2
Pyrite	< 0.5	0	< 0.5	< 0.5	7	4	2	< 0.5	0	0
Anatase	4	1	3	1	2	1	5	1	3	1

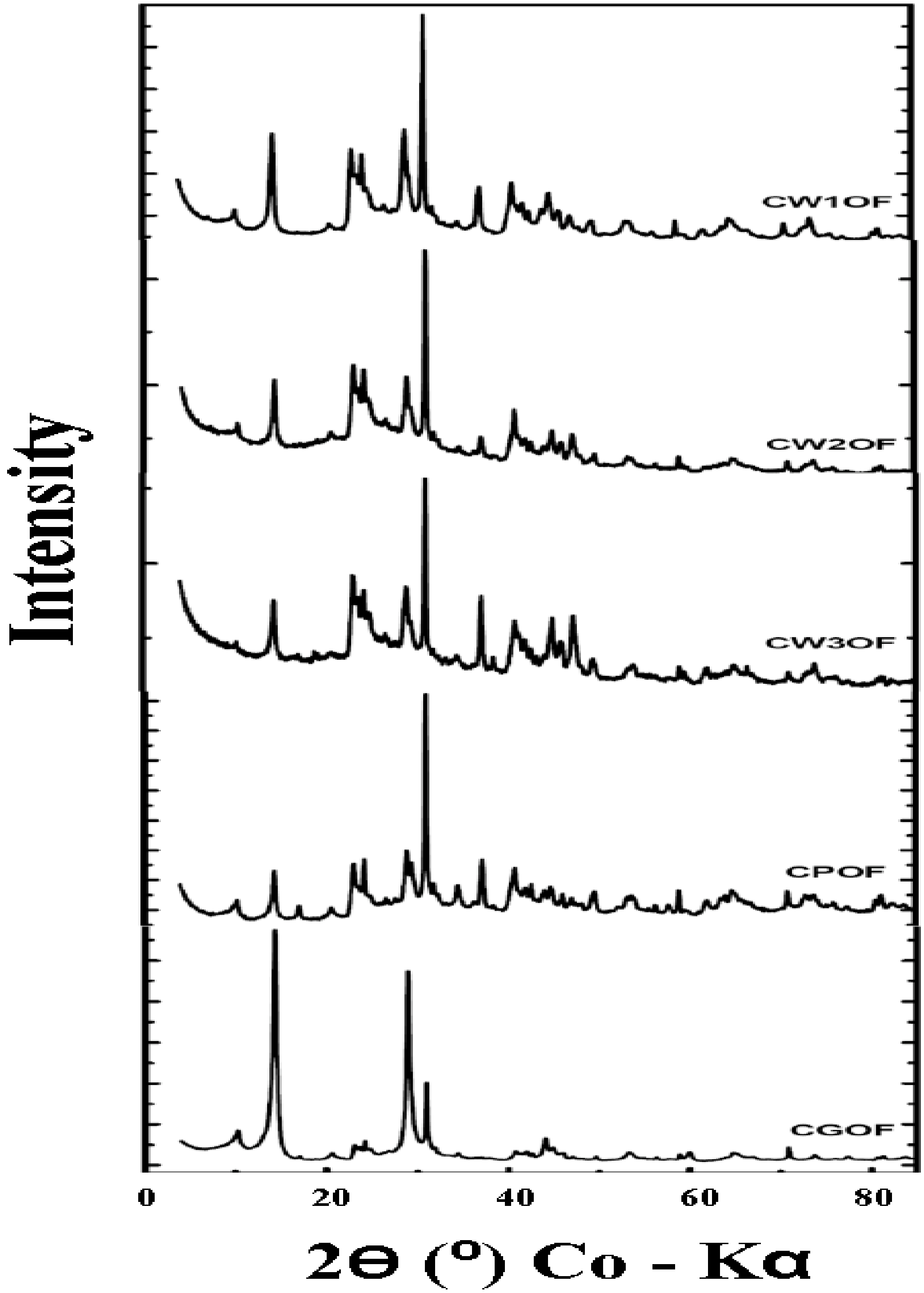

Figure 4.1: X-ray Diffraction Patterns of Isolated Solids (Clay Fraction) from the Bitumen Froth

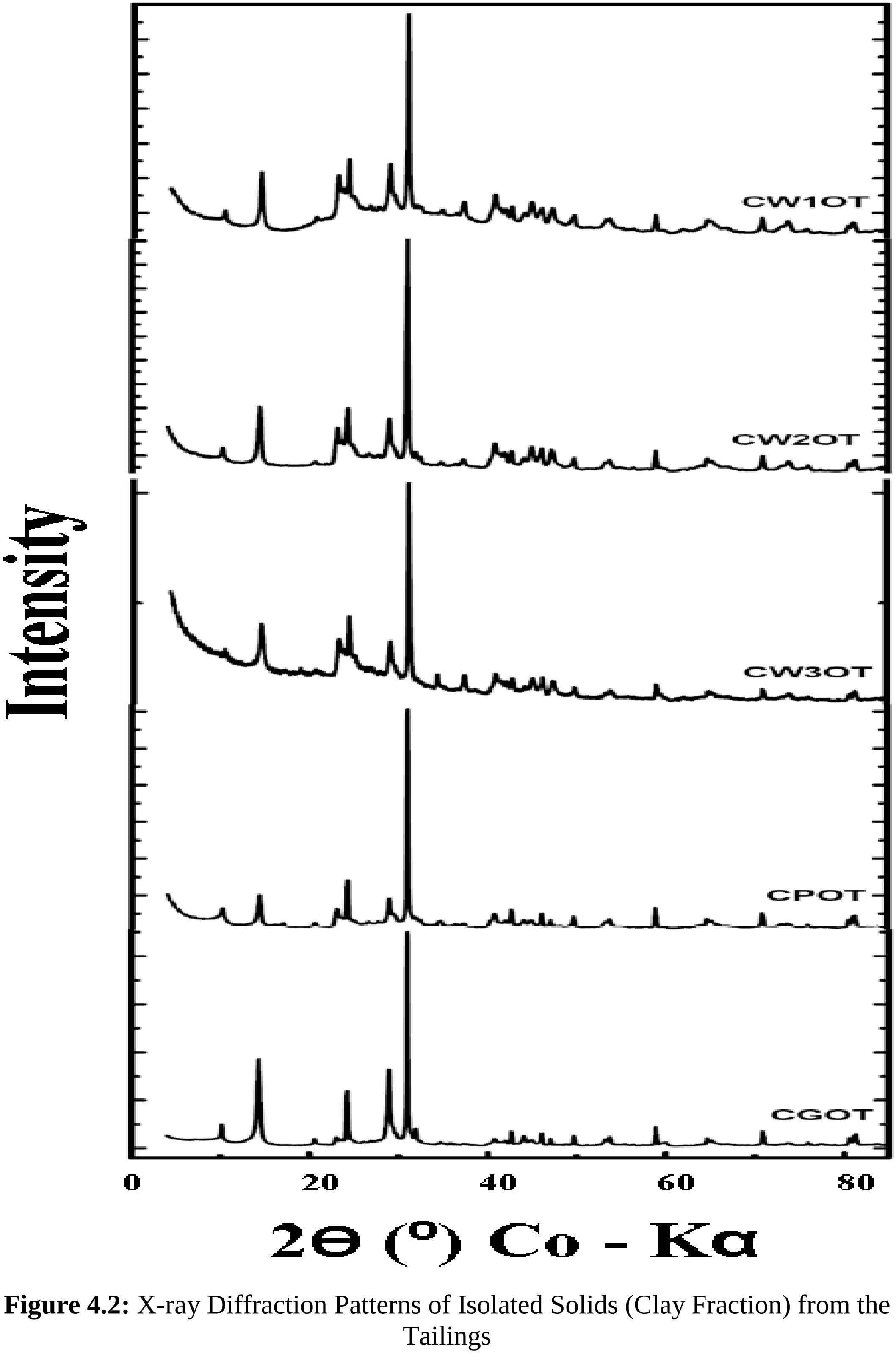

Figure 4.2: X-ray Diffraction Patterns of Isolated Solids (Clay Fraction) from the Tailings

clay fraction of ore G for both froth (CGOF) and tailings (CGOT). In addition, the high fines ore (P) has the lowest kaolinite to illite ratio in both the clay and silt fractions, in contrast to the other ores. The solids from the bitumen froth have more carbonates in the clay fraction and more clay minerals (kaolinite and illite) in the silt fraction when compared with those from the tailings. However, the tailings samples contain more quartz, which is not unexpected given that quartz is the most abundant mineral in the ores while clay minerals are enriched in the clay size fraction.

4.3.3 Energy Dispersive X-ray Analysis

The elemental composition of the samples determined by EDX is presented in Table 4.4. It can be observed that the isolated solids from the bitumen froth are richer in sulphur and transition metals – iron and titanium; than those from the tailings. This noted trend confirms the XRD results which suggested the presence of more iron carbonate (siderite) in the solids isolated from the bitumen froth than from tailings, particularly for the weathered and high fines ores. The presence of iron and titanium could also come from their oxides and hydrous oxides since GOF is deficient in siderite but has more iron and titanium than GOT. In their study, Kaminsky et al.[26] observed the presence of a large variety of iron – titanium compounds in the coarse solids extracted from bitumen froth, with iron compositions ranging from a few percent to stoichiometric ilmenite. Moreover, Stevenson[13] reported a mechanism of OM adsorption by the formation of strong coordination bond and simple anion exchange with hydrous oxides of iron and

Table 4.4: Elemental Composition of Isolated Solids by EDX

Element	**Samples (Atomic wt.%)**									
	W1OF	**W1OT**	**W2OF**	**W2OT**	**W3OF**	**W3OT**	**POF**	**POT**	**GOF**	**GOT**
Mg	2	2	1	1	1	1	2	1	0	0
Al	25	23	23	18	21	20	16	16	25	15
Si	43	60	52	66	37	60	38	72	61	74
P	1	0	0	0	1	0	1	0	0	0
S	3	2	7	3	6	3	3	2	4	3
K	2	4	3	3	2	3	3	4	2	5
Ca	2	1	1	0	1	1	2	0	1	0
Ti	4	2	4	2	2	1	9	2	3	1
Cr	<0.5	0	0	0	0	0	<0.5	0	0	0
Mn	1	0	<0.5	0	1	0	1	0	0	0
Fe	17	7	9	7	29	13	24	4	5	2

aluminium. This adsorption dominates surface reactions and induces a cementation effect that leads to the development of strong aggregation, formation of concretion and crust[13,19,20]. In addition, the higher sulphur content could contribute to a higher OM content in the isolated solids from the froth.

The samples from the tailings contain more silicon than the solids from the bitumen froth. This finding agrees well with the results of the XRD analysis which indicates the presence of more quartz in the isolated solids from the tailings.

4.3.4 Elemental Analysis

The total carbon, hydrogen, nitrogen and sulphur content determined by elemental analysis is given in Table 4.5. It can be seen that the solids isolated from the bitumen froth possess more of these elements than those from the tailings. This finding suggests that the solids in bitumen froth contain more carbonates, sulphides and adsorbed OM than the tailings samples. Such an observation agrees with the results of XRD analysis and elemental analysis by EDX.

A close look at the solids from the bitumen froth shows that the solids isolated from bitumen froth of high fines ore (POF) possesses the highest amount of carbon, while the solids isolated from the bitumen froth of low fines ore (GOF) are of the the lowest content of carbon. W3OF contains the most significant amount of sulphur amongst all the ores tested.

Table 4.5: Elemental Analysis of Isolated Solids

Sample	**Elements (wt.%)**			
	N	**C**	**H**	**S**
W1OF	0.35	18.69	2.42	2.02
W1OT	0.10	3.34	0.62	0.78
W2OF	0.45	18.06	2.30	2.34
W2OT	0.16	6.55	0.99	0.97
W3OF	0.35	17.34	2.08	4.19
W3OT	0.17	7.91	1.06	2.85
POF	0.43	21.66	1.97	1.78
POT	0.14	4.64	0.76	0.90
GOF	0.38	12.19	1.94	1.97
GOT	0.12	5.33	0.81	1.19

4.3.5 Infrared Spectra

The infrared spectra of the solid samples were divided into two spectral regions. Figure 4.3 covers a spectral region from 3700 to 1200 cm^{-1}, while Figure 4.4 depicts the spectra from 1200 to 600 cm^{-1}. The spectra in Figure 4.3 show that all the isolated solids exhibit the characteristics bands of aliphatic hydrocarbons – methyl and methylene groups at 2945, 2924, 2864, 2852, 1470 -1440 and 1377

cm^{-1} – in which the bands at 2924 and 2852 cm^{-1} are the most intense. Presence of ketones (aromatic and aliphatic) can be seen in the broad bands at 1700-1650 and 1637-1552 cm^{-1}. The presence of carboxylic acids is inferred from IR bands at 3300-3000 cm^{-1} (broad band) and 1710-1680 cm^{-1}. Furthermore, the presence of carboxylate is identified by the bands between 1610-1560 and 1400-1310 cm^{-1}.

Overall, these bands are more intense for the samples from the bitumen froth than from the tailings, indicating more OM on the solids in bitumen froth. The presence of carboxylic acid and carboxylate indicates that the OM on solids is likely from the surface active organic molecules binding on the solids through their functional groups to make the solids hydrophobic. This observation confirms the results obtained from the EDX and elemental analysis, showing more organic matter with which elemental carbon, hydrogen, nitrogen and sulphur are associated.

The carbonate bands at 1802, 1438 – 1415 and 862 – 864 cm^{-1} observed for the weathered and high fines ores in both Figures 4.3 and 4.4 are attributed to the presence of siderite. For the low fines ore the characteristic bands for calcite (1435 - 1410 cm^{-1}) was seen in the sample from the bitumen froth (GOF). It appears that the carbonates preferentially distributed in the bitumen froth of oil sands, which is characterized by a distinctive amount of OM in contrast to the tailings. The results from the XRD, EDX and elemental analysis validate this trend.

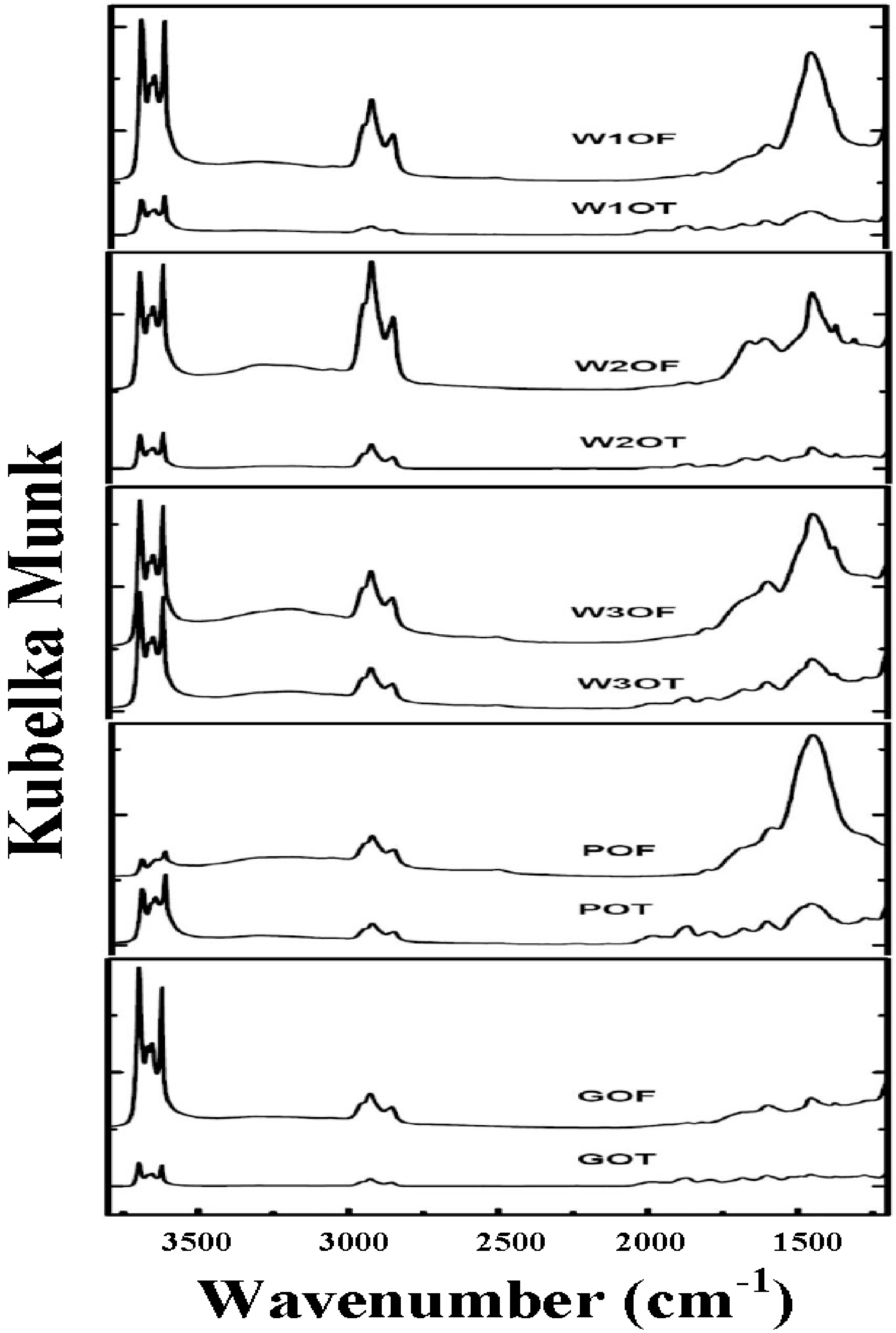

Figure 4.3: Infrared Spectra of Isolated Solids (3700 – 1200 cm^{-1})

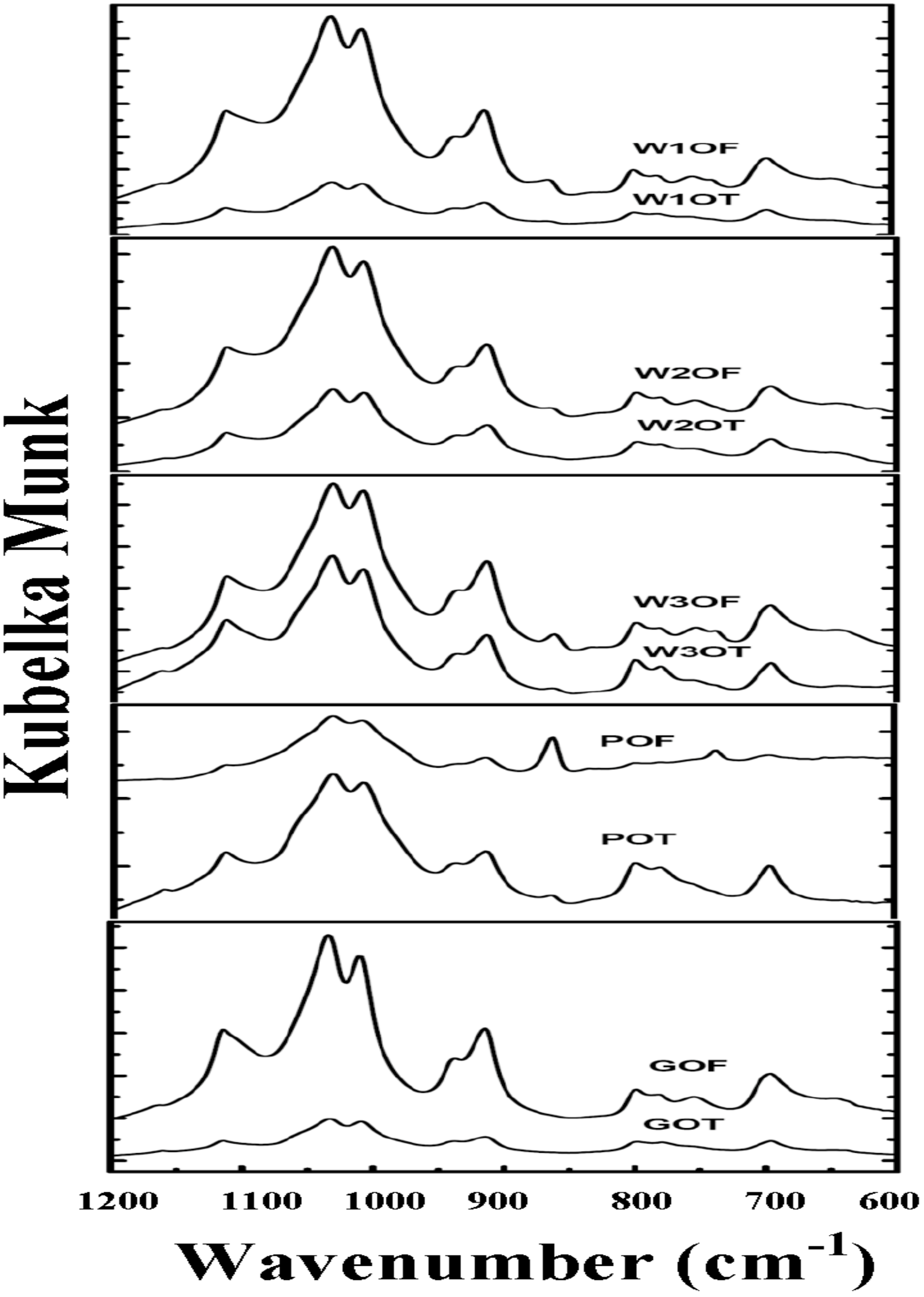

Figure 4.4: Infrared Spectra of Isolated Solids (1200 – 600 cm^{-1})

The presence of more carboxylic acid salts in the bitumen froth than tailings also supports this trend. These salts are surfactants used as collectors in traditional froth flotation, which could have possibly influenced the recovery of the carbonates into the bitumen froth.

The association of OM with carbonates was first postulated by Chave[21, 22] who observed the absence of chemical interaction between carbonates particles and sea water while studying suspended carbonate particles in surface sea water. This was attributed to the protection of the carbonate grains from the water by resistant organic coatings[22]. In a previous study of a low grade-high fines oil sands ore using solvent–extraction technique, Kotlyar et al.[6] proposed that siderite could be a major inorganic component in the organic-mineral complexation. In addition, Suess[21, 23, 24] demonstrated that carbonate grains preferentially adsorb surface – active OM from seawater. This association[24] was described as chemical and / or physical adsorption, the enclosure of the grains by mucilage sheaths and the adherence of living or dead bacteria and organic compounds to the carbonate minerals. Carter et al.[21] interpreted the association with carbonates to be due to the similarity between carbonate anions and carboxyl groups. In the study of oil shale bitumen, Vandergrift et al.[27] implied that carboxylic acids could be a possible linkage between organic matter and carbonate.

The presence of clay sized minerals is reflected by the presence of distinct sharp bands from 3800 to 3600 cm^{-1} which correspond to hydroxyl groups associated with alumina as shown in Figure 4.3. The presence of bands at 1161, 1112, 1030, 1009, 799, 782, 754 and 698 cm^{-1} for Si – O stretching and 935 and 914 cm^{-1} for Al – OH deformation in Figure 4.4 further confirms the presence of alumino-silicates. These minerals are mainly kaolinte, illite and quartz (1161, 799, 782, 698) as revealed in the XRD patterns.

4.3.6 Bitumen Recovery

The bitumen recovery as a function of flotation time is shown in Figure 4.5. It can be observed that the low fines ore (G), which has a low amount of organic coated solids, features the highest bitumen recovery while W1 of the highest amount of organic coated solids has the lowest bitumen recovery. Figure 4.6 depicts a plot of the bitumen recovery obtained in the first 10 minutes of flotation after 5 minutes of conditioning as a function of percent of organic coated solids present in the oil sands. The first 10 minutes of flotation was used by Dang-Vu et al.[28] to illustrate the relationship between the wettability of solids extracted from oil sands tailings and bitumen recovery. Hence, this was utilized in this study as a basis. This plot illustrates the effect of the presence of organic coated solids on bitumen recovery. It can be noted that as the amount of organic coated solids increases the bitumen recovery decreases. Overall, the results are consistent with the observation made by Dang – Vu et al.[28] that weathered ores possess the least amount of water – wet particles and the lowest bitumen recovery in comparison to other types of oil sand ores. The results from this study further reinforce the critical role of solids wettability in controlling processability of oil sands ores.

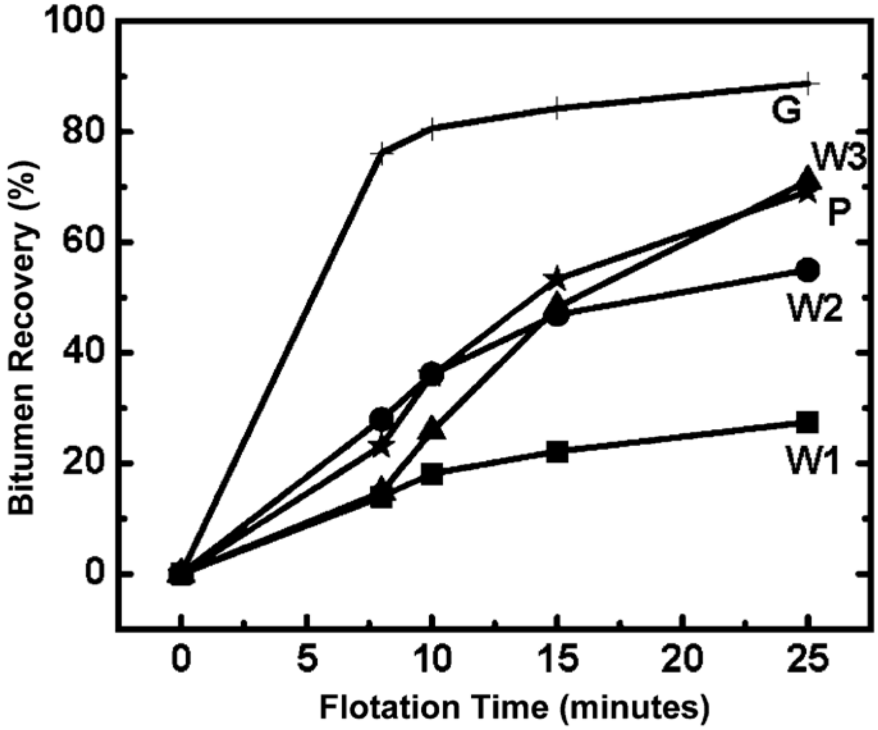

Figure 4.5: Bitumen Recovery vs. Flotation Time

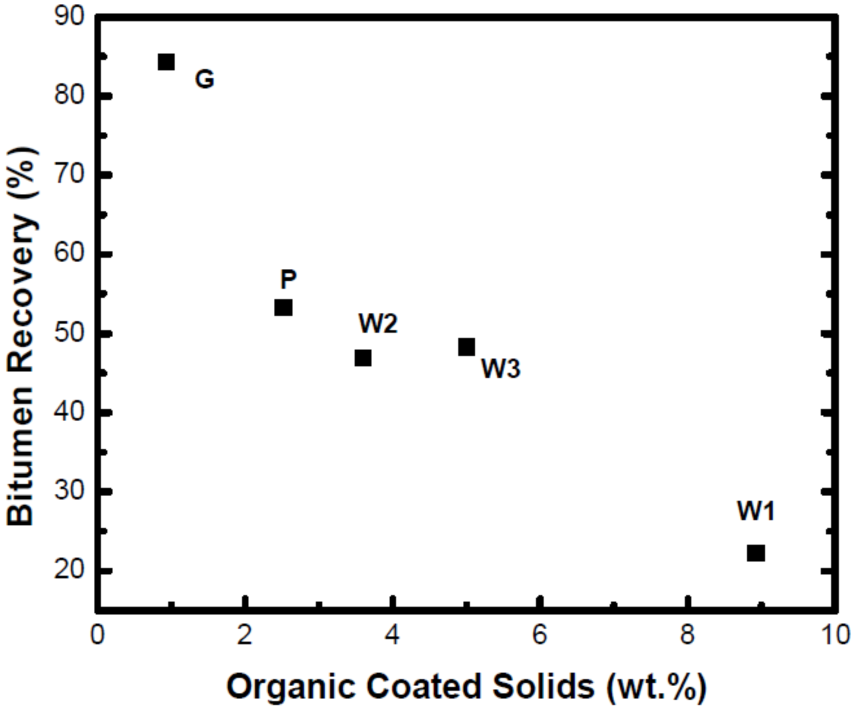

Figure 4.6: Relationship between Bitumen Recovery and Percent Organic Coated Solids Content of the Oil Sands

4.4 Summary

Organic coated solids isolated from the bitumen froth of the different ores are observed to possess more clay minerals and associate more with carbonates, transition metals and probably oxides and hydrous oxides of iron and aluminum as implied by the infrared spectra results and confirmed by XRD, EDX and elemental analysis. The association with carbonates could be due to the similarity between carbonate anions and carboxyl groups as explained by Carter et al.[21].

Moreover, most of the quartz minerals are observed to preferentially distribute in the tailings than in the bitumen froth. More organic coated solids are found in the weathered oil sands than in the other types of oil sand ores. The presence of organic coated solids is observed to reduce bitumen recovery from oil sands.

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CHAPTER FIVE

CHARACTERIZATION OF WEATHERED OIL SANDS ORES[§]

5.1 Introduction

Oil sands contain connate (formation) water and mineral solids impregnated with bitumen. One of the largest reserves of oil sands deposits in the world is found in Northern Alberta, Canada and is estimated to contain 1.7 trillion barrels of crude bitumen[1]. Oil sands ores are generally classified[2] by their bitumen content as high grade ore (of over 12 wt. % bitumen content), average grade ore (characterized by 9 to 12 wt. % bitumen content) and low grade ore (of less than 9 wt. % bitumen content). A high bitumen recovery is usually obtained from the high grade ore but this is seldom the case for one particular type of ore[3-14] described as being “weathered”, “oxidized” or “degraded”. Despite a high bitumen content (>12 wt.%) and low fines (<45 µm) content, this type of ore exhibits extremely poor processability with low bitumen recovery and poor bitumen froth quality.

The weathered ores exist at a close proximity to the boundary of the overburden and oil sand formation[3]. Ren et al.[14] described this ore as being exposed to the environment for an extended period of time and not being deeply buried under the overburden. Mikula et al.[5] showed that the bulk of this type of ores can be found within 12 m of the surface. They reported that a significant amount of ore outcropping at an escarpment adjacent to the Athabasca River had little or no

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[§] This chapter is based on: Adegoroye, A; Srinivasa, S.; Omotoso, O.; Xu, Z.; Masliyah, J. *Appli. Clay Sci.* **2010** (in review).

overburden cover. Hence, it is not surprising that weathering of the oil sands occurs due to their exposure to the environment (water, oxygen, carbon dioxide and organic compounds).

According to Bohn[15], weathering involves the movement of water through the soil profile and gradual removal of mainly silica, alkali and alkaline earth cations. Thus, the crystal structures and ion valences of rocks exposed at the earth's surface become unstable due to physical and chemical processes. The major reaction that weathers minerals is the strong tendency of ions in solids to dissolve in water[15]. Weathering ensures the development of soil and the weathered rock is usually referred to as the parent material in which the mineral soils form[16]. Soils may also contain the unweathered minerals residual from the parent material as well as the minerals that weathering produces[16]. The major weathering products are the clay minerals which stick to one another and other particles[16]. Clay particles reflect the soil's chemistry as sand and silt particles are largely vestiges of the parent rock[16, 17]. At different stages of weathering, different clay minerals are altered, decomposed and recrystallized[17]. Therefore, a study of the mineralogy and properties of weathered oil sands could provide a better understanding of its processability.

The poor processability of weathered ores is often not related to the amount of fines or clay content, which is used as markers of processability by oil sands operating companies[5]. Previous studies[4-6,9] proposed that the poor processability of weathered ores could be due to the change in bitumen chemistry or oxidation of minerals in the ores. Chemical markers that imply oxidation of oil sands ores such as low pH and/or the presence of soluble divalent cations such as Mg^{2+} and Ca^{2+}, have been cited by several authors[4-6,9]. Mikula et al.[5] reported that some weathered ores do not show these chemical markers and proposed that in this instance the nature of the bitumen determines bitumen extraction recovery. A higher quantity of organic-wet solids in weathered ores has been reported in a number of previous studies[18, 19]. According to Ren et al.[14], the wettability of solids in weathered ores serve as a better indicator of processability than bitumen and fines content.

The objective of this study is to present a detailed characterization of three weathered oil sand ore samples from mainly a mineralogical perspective and correlate the results to their processability. To determine the limiting step in bitumen recovery, liberation of bitumen from the weathered oil sands ores was studied using a flow visualization cell incorporated with a stereo-optical scope and a high resolution digital camera interfaced with a computer, recently designed and constructed at the University of Alberta.

5.2 Experimental

5.2.1 Extraction of Solids

Three different oil sands ores with varying degrees of weathering and two unweathered ores with high and low fines content were used in this study. The weathered ores coded as “W1” and “W2” were from Suncor Energy Inc. and “W3” from Syncrude Canada Ltd., while the high fines ore (“P”) and low fines ore (“G”) were from Syncrude Canada Ltd. and Suncor Energy Inc., respectively. Two different methods were used for separating the solids from bitumen and formation water. In the first method, Dean Stark extraction using toluene was used to remove bitumen from the oil sands, while the second method involves the isolation and partitioning of solids from the bitumen froth and tailings after warm – water extraction by a Denver flotation cell.

5.2.1.1 Dean Stark Extraction of Solids

The Dean Stark apparatus used for separating solids from bitumen and formation water in oil sands consisted of a heater and a round bottom – flask connected to a condenser with a trap / receiver. For each analysis, three different thimbles were each filled with 50 g of oil sands. Each thimble was placed in a wire mesh which was hung in the flask containing approximately 200 mL of pure toluene. The flask was placed in a bowl-like heater and connected to a condenser with a graduated trap. The cold water was allowed to flow through the heat exchanger and condenser to condense the steam and toluene vapour. The heater was switched on to vaporize the liquids and reflux through the oil sands sample.

The reflux continued for 30 minutes at which the dripping toluene became colorless. During refluxing, the formation water in the oil sands samples also vaporised, and was collected in the graduated trap after being condensed in the condenser. At the end of the refluxing, the bitumen-free solids in the thimbles were placed in a vacuum oven to dry for over twelve hours. Dried solids were labeled as DW1, DW2 and DW3 for weathered W1, W2 and W3 oil sands ores, respectively, and DP and DG for unweathered high and low fines ores, respectively.

5.2.1.2 Liquid – Liquid Extraction of Oil Sand Solids

The procedure for extracting the solids from the different oil sand ores using liquid-liquid extraction method has been described in our previous communications[19, 20]. It is presented in Figure 5.1 and described below.

To liberate bitumen from the oil sands (conditioning), 300 g of ore was placed in a Denver flotation cell and agitated at 1,500 rpm in 950 mL of warm deionised water at 35°C for 5 minutes. After conditioning, 150 ml/min air was introduced into the slurry to float the liberated bitumen. The bitumen froth was skimmed off from the surface of the slurry and collected in a jar. This process continued for 20 minutes after which 250 mL of heptol (heptane:toluene at 2:1 volume ratio) was added to the remaining slurry (tailings) of the Denver flotation cell and agitated for 5 minutes. The agitated slurry was collected and transferred into a separating funnel where solids partitioned into organic and aqueous phases.

The separated organic phase slurry from the heptol – tailings mixture was centrifuged at 20,000 g for 20 minutes and the supernatant was removed by

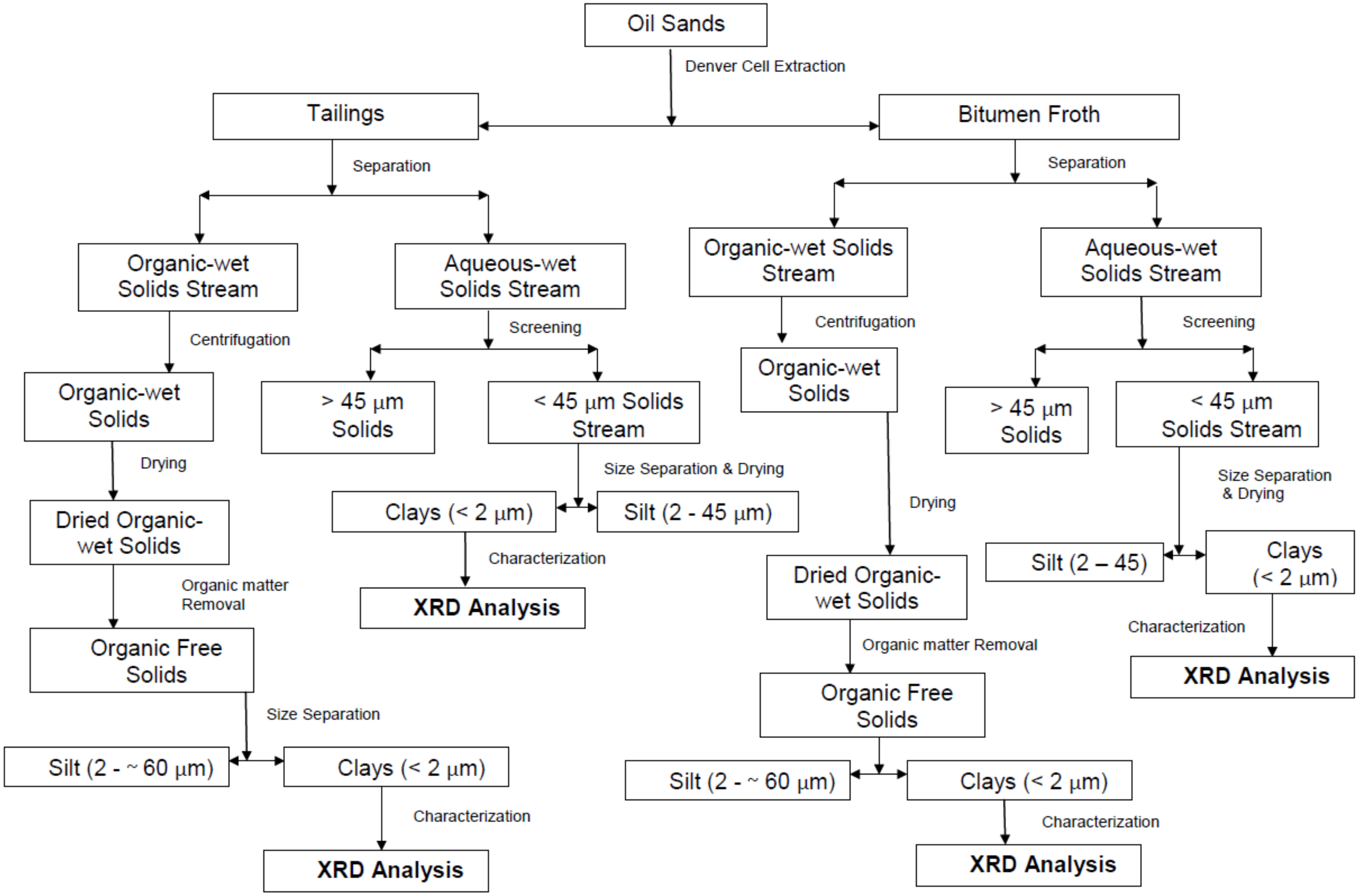


Figure 5.1: Liquid – Liquid Extraction of Oil Sand Solids

decantation. The solids that were formed at the bottom of the centrifuge tubes after the centrifugation process were washed and centrifuged with heptol solvent to remove residual bitumen until the supernatant became clear – indicating complete removal of bitumen.

The aqueous phase from the separating funnel was wet-sieved into distinct size fractions and the <45 µm solids in the slurry were concentrated by centrifugation at 20,000 g. All the solids obtained were subsequently dried under vacuum at 25^{o}C for 1-2 weeks.

The solids partitioned in the aqueous phase from the tailings of the weathered (W1, W2 and W3), high (P) and low (G) fines oil sands ores are designated as WW1T, WW2T, WW3T, WPT and WGT respectively. While solids partitioned in the organic phase were labeled as OW1T, OW2T, OW3T, OPT and OGT.

The recovery of the solids from the bitumen froth proceeded with the addition of 250 mL of heptol solvent in the jar containing the bitumen froth. The mixture was agitated in a shaker for 22 h. After settling for 30 minutes, the mixture was separated into organic and aqueous phases. The solids within each phase were processed in the same manner as used for the tailings slurry described above.

The solids isolated from the aqueous phase of the bitumen froth of the weathered (W1, W2 and W3), high (P) and low (G) fines oil sands ores were labeled as

WW1F, WW2F, WW3F, WPF and WGF respectively. While the solids partitioned in the organic phase were labeled as OW1F, OW2F, OW3F, OPF and OGF, respectively.

For x -ray diffraction analysis, clay sized minerals were separated from the rest of the isolated solids (after the removal of organic matter for oil wet solids). Letter "C" or "S" was placed in front of the sample codes above to indicate their fractions as clay (<2 µm) or silt (2-45 µm). For instance, CDW1 refers to clay samples from the solids extracted from weathered ore W1 by Dean stark extraction, while COGF refers to oil-wet clay samples from the bitumen froth of the low fines ore.

5.2.2 X-ray Diffraction Analysis

A Bruker D8 Advance x-ray diffractometer, equipped with an incident beam parabolic mirror, cobalt radiation (CoKα) and a linear detector (VANTEC-1^{TM}), was used to obtain the diffraction patterns of the clay (<2 µm) and silt (2-45 µm) particles of the samples. The oriented clay slides and random powder clay samples were prepared for analysis.

Calcium-saturated oriented-clay slides were prepared with the Millipore filtration method as described by Moore and Reynolds[21] to obtain the 00*l* diffraction pattern of the clays. This analysis is to facilitate the identification of mixed–layered clays present in the samples. In this method, a suspension of well dispersed clay-sized minerals (CSM) in deionised water was poured into a vacuum filter apparatus (Model, Millipore) containing a 0.45 µm filter paper. After filtration, 10 mL of 0.1 M calcium chloride solution was added to the formed filter cake to enable an exchange of Ca^{2+} ions in the interlayer of the clays. The filter cake was washed with deionised water to remove the Cl^- ions and excess Ca^{2+} ions.

The clay cake formed on the filter paper was transferred onto a 25 mm quartz slide by placing the moist filter paper with clay onto it. After air-drying, the dry clay slides were placed in a desiccator containing a saturated solution of magnesium nitrate to ensure that the clay samples were at high relative humidity (RH). The *00l* diffraction patterns at high RH were obtained from $2\Theta = 5^0$ to 35^0. The slides were then treated with ethylene glycol in a sealed desiccator placed in an oven for 24 h at 65^oC. The slides were then analyzed again after cooling at ambient temperature for at least an hour.

Sample preparation methods for XRD analysis of the random powder was described by Omotoso et al.[22]. Briefly, CSM were sieved onto a quartz sample holder to ensure that they were not lumped up together. While for the analysis of the silt, the samples were ground in 5 mL of methanol with a McCrone mill and agate balls placed in a 100 mL jar for 7 minutes. The purpose of grinding the samples was to reduce the particle size of the silt so that the bigger quartz particles would not overshadow the smaller minerals. To obtain a well dispersed powder sample, the ground silt went through a milling process by a Retsch

MM301 mixer mill in a 10 mL jar with plastic balls for 10 minutes. The resulting samples were sieved onto a quartz sample holder and levelled while trying to avoid preferential orientation of the samples. Diffraction patterns for the randomly oriented samples were obtained from $2\Theta = 4^{0}$ to 85^{0}.

The procedure for quantitative analysis of oil sand clays from oriented slides using NEWMOD^{TM} and TOPAS^{TM} has been previously described by Kaminsky et al.[4]. Oriented, 1-dimensional diffraction patterns for glycolated, calcium-saturated pure clays were simulated using NEWMOD^{TM}. Subsequently, TOPAS^{TM} was used to obtain the peak positions and integrated intensities of the resulting simulated profiles. These parameters were used in quantifying the mixed layered and regular clays identified by the NEWMOD^{TM} derived model using the mineral intensity factor (MIF) as described by Moore and Reynolds[2]. The peak position and areas of the measured (experimental) diffraction patterns of the samples were likewise determined using TOPAS^{TM}. The clays that were considered for quantification include kaolinite (001), illite (002), kaolinte-smectite (001) and illite-smectite (002/003). In this study, illite (002) of the pure clay profile from NEWMOD^{TM} was used as the reference model clay.

$$\mathrm{MIF_i} = \mathrm{I_{p,i}} / \mathrm{I_{p,s}}$$

$$\text{Weight \% of i}^{\text{th}}\text{clay} = \frac{(\mathrm{I_i} / \mathrm{MIF_i})}{\left(\sum_{i=1}^{n}(\mathrm{I_i} / \mathrm{MIF_i})\right)} \mathrm{x}100$$

where $I_{p,i}$ and $I_{p,s}$ are the single peak intensity calculated using TOPAS^{TM} from NEWMOD^{TM} derived pure clay profiles of the ith modelled clay phase and a reference model clay phase (illite (002)), respectively. I_i is the peak area of the ith clay phase.

The mineral phases in the random powder sample of clay-sized minerals (CSM) and silt were quantified with TOPAS^{TM}. The quantification was based on multiphase structure refinement (Rietveld) to give the weight percent of the minerals present. Model structures were taken from the Inorganic Crystal Structure Database (ICSD).

5.2.3 Surface Area

The surface area (SA) of the clay minerals was estimated from the results of XRD and methylene blue (MB) adsorption analysis. For SA analysis from XRD results, the methodology used by Nadeau[24], Omotoso et al.[25] and Kaminsky et al.[23] was adopted. This method uses the fundamental thickness of the clay particles – kaolinite, kaolinite-smectite, illite and illite-smectite to evaluate SA for each clay mineral. The total SA of the samples was determined from the quantitative XRD analysis.

The MB adsorption method is based on the determination of cation exchange capacity (CEC) of clay minerals, as proposed by Hang and Brindley[26]. This method has been used in our previous communication[20]. The SA is related to the CEC through the following equation[26].

$$\mathrm{SA}\ \left(\mathrm{m}^2/\mathrm{g}\right) = \mathrm{CEC}\ \left(\mathrm{from\ MB}\right) * 130 * 0.0602$$

5.2.4 Bitumen Liberation Analysis

The experimental setup for the bitumen liberation test is shown in Figure 5.2. This novel set-up consists of a flow visualization cell designed for the bitumen liberation process from oil sands ore and a stereo-optical microscope equipped with a high resolution digital camera. The digital camera transfers high quality images to a computer screen. The flow visualization cell consists of a sample holder with a glass frit on the bottom. A thin layer of vacuum distillation unit feed bitumen is spread on a filter paper of the same dimensions as the glass frit. A small lump of oil sand sample is pressed onto the bitumen-smeared filter paper placed in the sample holder. The excess oil sands sample is carefully removed from the top using a knife to obtain a flat surface of oil sands to be exposed to flowing process fluids. The sample holder is then sealed by a Teflon o-ring under the clamps and connected to a low level vacuum line. The vacuum is used to hold the oil sands samples in place. The cell is sealed from the top with a glass slide in a cover plate. A set of baffles is provided at the exit end of the fluid to prevent eddy formation inside the cell. Process water of pH 8.5 from Syncrude Canada Ltd., maintained at 35°C with a water bath, was pumped into the visualization flow cell with a peristaltic pump while the images were recorded by computer at desired 100 milliseconds image capture speed.

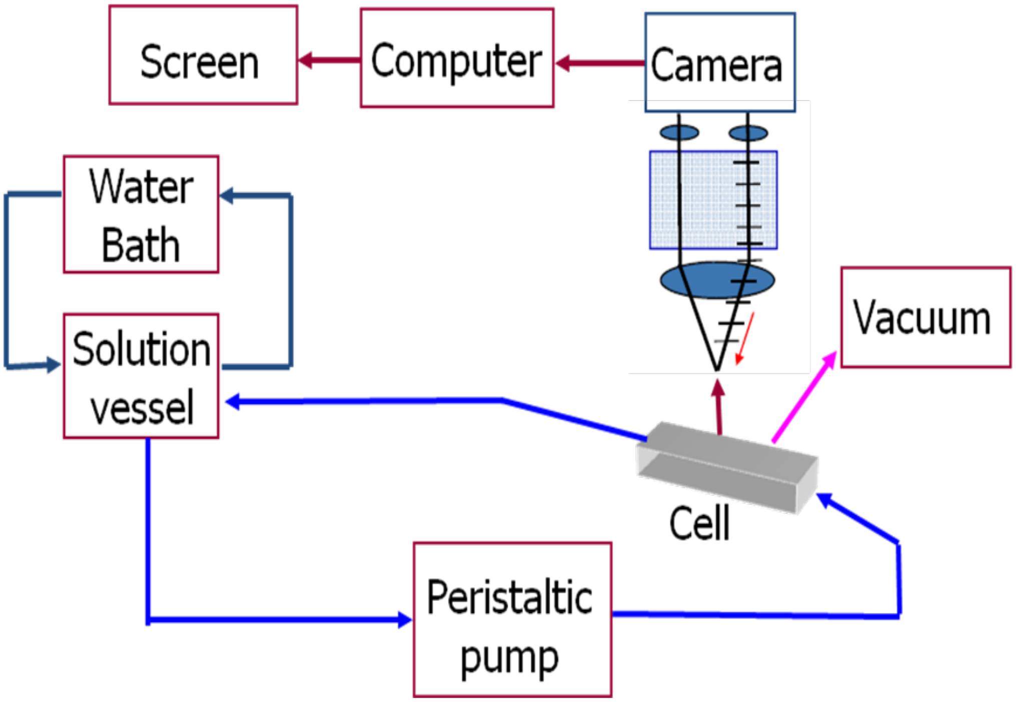


Figure 5.2: Experimental Set-up for Bitumen Liberation Test

As the bitumen film on the sand grains starts to recede under the liquid flowing over them to form bitumen droplets on the sand grains, it is necessary for the oil sand grains to remain intact without the slightest displacement to obtain real time, high quality images under the stereo-optical microscope. The vacuum line is intended to hold the oil sand in place on the sample holder. The entire bitumen liberation process recorded with a high resolution camera is analyzed off-line.

5.3 Results and Discussion

5.3.1 Overview of Oil Sands Properties

Table 5.1 summarizes the property of oil sand ores used in this study. The values are within an error of ±0.3 by standard deviation. It can be seen that the weathered ores (W1, W2 and W3) and low fines ore (G) have high bitumen content (above 12 wt. %) and are referred to as high grade ores. The high fines ore (P) contains less bitumen (less than 10 wt. %) in comparison with the other ores and is referred to as an average grade ore. The formation water analysis of these ores shows that the weathered ores are more acidic (pH less than 6.5 %) than the other types of ores. The divalent ion content of the weathered ores is higher than those of the high and low fines ores. Ore W3 contains a much higher amount of the divalent ion content (75 ppm Ca^{2+} and 16 ppm Mg^{2+}) and possesses the lowest pH (5.1) than the other ores. The clay content of ores W3 and G is approximately the same.

The bitumen recovery kinetics and bitumen to solids ratio of the oil sands ores during bitumen extraction tests using the Denver flotation cell are presented in Figures 5.3 and 5.4, respectively. Low fines ore G exhibits the highest bitumen recovery and bitumen to solids ratio, while weathered ore W1, displayed the lowest bitumen recovery and bitumen froth quality. It was observed that the bitumen froth from the weathered ores is of a higher bitumen froth density.

5.3.2 Particle Size Distribution of Solids

The particle size distribution (PSD) of the solids in the weathered (W1, W2 and W3), high (P) and low (G) fines oil sands ores is shown in Figure 5.5. It is evident

Table 5.1: Properties of Oil Sand Ores

Oil Sands Ore	Composition (wt.%)					Formation Water Chemistry			
	Bitumen	Water	Total Solids (including fines)	Fines in Oil Sands (<45 µm)	Clay Content (<2 µm)	pH	Calcium (Ca) (mg/L)	Magnesium (Mg) (mg/L)	Hardness ($CaCO_3$) (mg/L)
W1	**14.5**	**1.0**	**84.5**	**8.8**	**4.4**	**6.4**	**6.5**	**4.5**	**35**
W2	**12.2**	**2.6**	**85.2**	**5.9**	**2.6**	**5.6**	**6.8**	**5.7**	**41**
W3	**12.0**	**1.0**	**87.0**	**4.1**	**1.7**	**5.1**	**75.0**	**16.0**	**250**
G	**15.9**	**1.5**	**82.6**	**2.6**	**1.5**	**6.7**	**0.9**	**3.6**	**17**
P	**9.6**	**3.4**	**87.0**	**18.0**	**5.6±0.6**	**8.0**	**2.9**	**2.1**	**16**

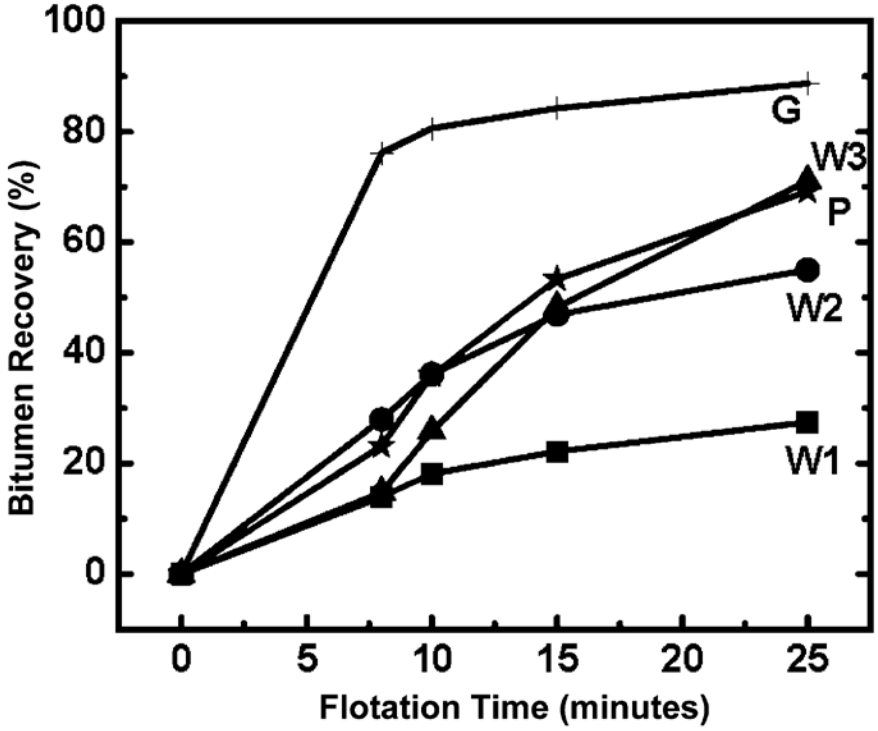


Figure 5.3: Bitumen Recovery vs Flotation Time

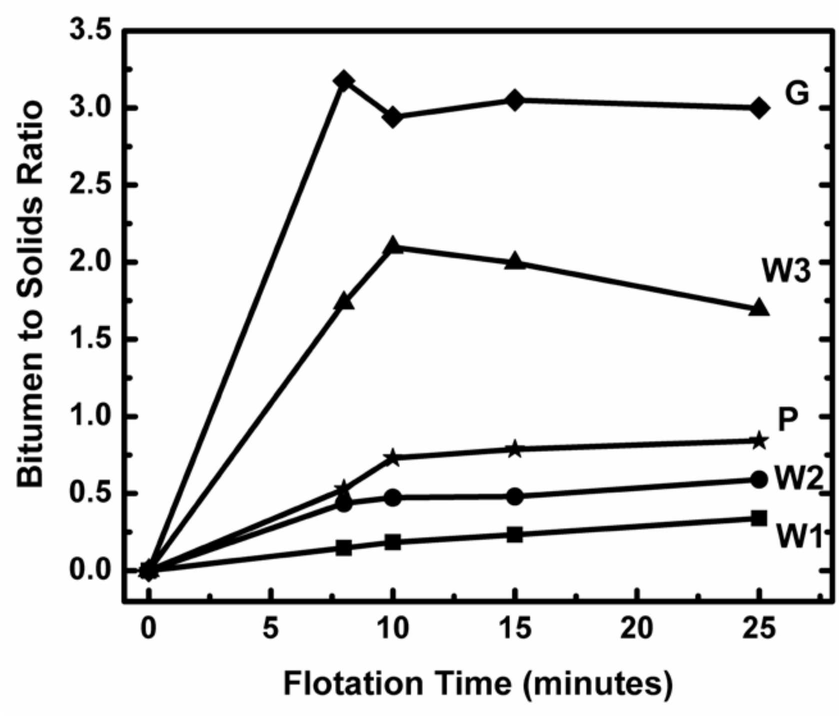


Figure 5.4: Bitumen to Solids Ratio vs Flotation Time

that solids in ores W3 and G have very similar PSD, containing very low fines content, and the solids are mostly greater than 212 µm. Majority of solids in ores P and W2 are within the size range of 106 – 212 µm. Most of solids in W1 are in the 45 – 106 µm size range. It is not surprising that ore P contains the highest percentage of fines as also shown in Table 5.1.

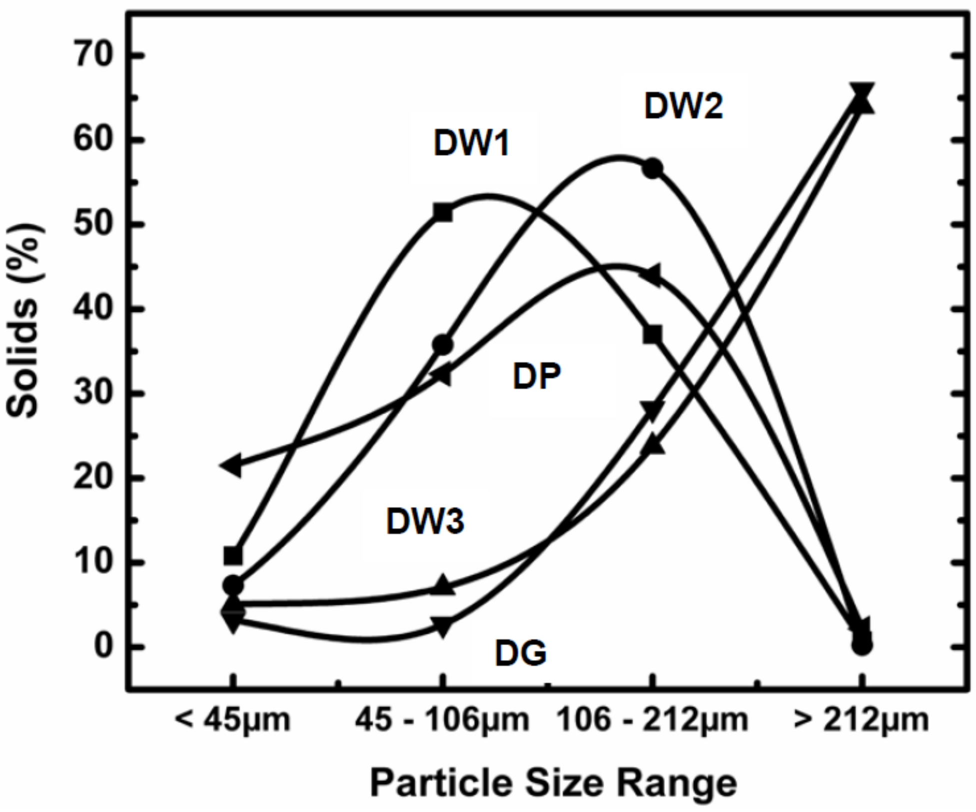


Figure 5.5: Particle Size Distribution of Solids in the Ores

5.3.3 Partitioning of Solids

The partition of solids between the aqueous and organic phases from the bitumen froth and tailings is presented in Figure 5.6. It is evident that solids are mostly distributed in tailings, more than 90 %. The bulk of the solids in the tailings are partitioned in the aqueous phase. The least amount of solids is distributed in the bitumen froth from ores W3 and G of similar PSD as compared with the other ores.

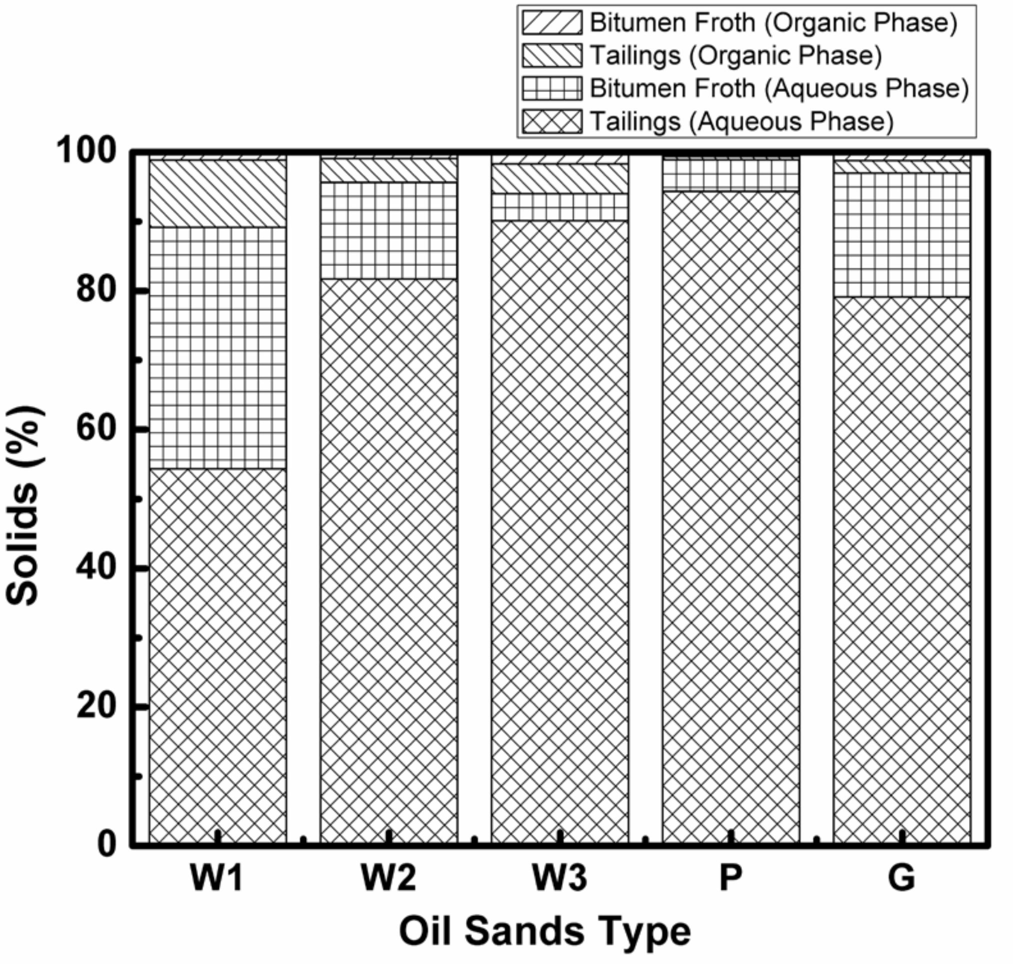


Figure 5.6: Distribution of Isolated Solids in Bitumen Froth and Tailings

It can be seen that the highest fraction of solids is partitioned in organic phase from ore W1 than any of the other ores, while the least fraction of solids is partitioned in the organic phase from ore G. It is evident that the weathered ores contain a higher fraction of solids partitioned in the organic phase when compared with the high and low fines ores. In connection with the results of bitumen recovery in Figure 5.3, it appears that lower wettability of solids (more partition in organic phase) leads to lower bitumen recovery of ores W1 and W3. Such a correlation between the wettability of solids and bitumen recovery has been reported by Dang-Vu et al.[18] and Adegoroye et al.[19].

5.3.4 X-ray Diffraction Result

5.3.4.1 Oriented Clay Slides

The clay minerals present in all the oil sands samples include illite, kaolinite and quartz as identified in Figure 5.7. It can be seen that weathered ores W1 and W2 possess chlorite which is absent in weathered ore W3, high (P) and low (G) fines ores. A significant amount of lepidocrocite was observed in only ore W3. Mixed layered clays observed in all the clay minerals extracted from different oil sands ores include illite-smectite and kaolinite-smectite.

Corrensite, defined as a 1:1 regular interstratification of trioctahedral chlorite with either trioctahedral smectite or trioctahedral vermiculite by Bailey[27], was found in the XRD patterns of weathered ore W1 and in the clay samples partitioned in the aqueous wet froth (CWW1F) from ore W1. The occurrence of this mixed layer clay has never been reported in previous studies of clays extracted from oil sands. According to De Kimpe et al.[28], corrensite has been known for many years[29-31] and could originate from a variety of geologic environments[31] including hydrothermal[33-36] and sedimentary[30,31, 37-39] origin as well as from synthetically oxidized chlorite[40].It is usually associated with chlorite and phlogopite[28] – a type of mica (illite and muscovite are also micas).

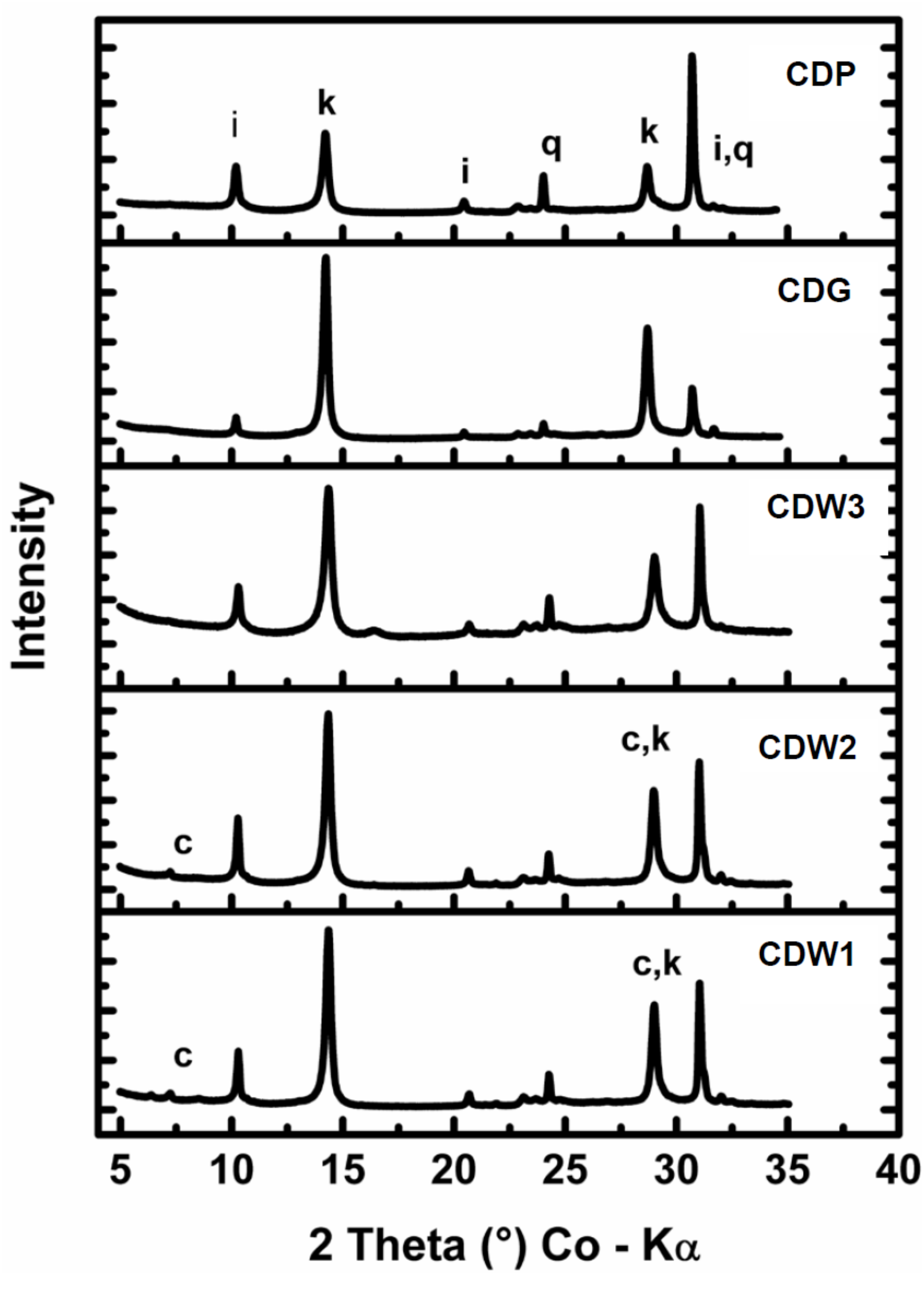


Figure 5.7: X-ray Diffraction Patterns of the Clay Minerals in the Different Oil Sands Ores (c – chlorite, i – illite, k – kaolinite and q – quartz)

Corrensite could be of lower charge if the chlorite is interstratified with smectite, or of high charge if the interstratification is with vermiculite[27]. In order to distinguish the type of corrensite present in ore W1, some diagnostic x-ray diffraction analysis was performed. In addition to the analysis of calcium saturated samples, the clay samples extracted from ore W1 was saturated with magnesium ions and treated individually with ethylene glycol (EG) and glycerol (GLY), respectively. Figure 5.8 shows XRD patterns of the treated clay samples from ore W1. When saturated with calcium ions (Ca), the treatment with EG caused an expansion from 14.5 Å as seen in the sample Ca-CWW1F, exposed to a high relative humidity (RH) to 16.2 Å for Ca-CWW1F and Ca-CDW1 treated with EG. The samples saturated with magnesium ions (Mg) when treated with EG and GLY was found to be resistant to expansion. It has been reported that when saturated with magnesium ions, a high charged corrensite is resistant to expansion[27]. It is therefore safe to conclude that the corrensite found in the clay samples extracted from weathered ore W1 is the high charged corrensite.

It is noteworthy that the corrensite in bitumen froth from ore W1 was only partitioned in the aqueous phase. In addition, ore W1 has the highest fraction of solids in bitumen froth partitioned in the aqueous phase as well as the highest solids fraction reported to bitumen froth. Further studies on corrensite and its parent rock or material may be required to determine its effect on the processability of oil sands ores.

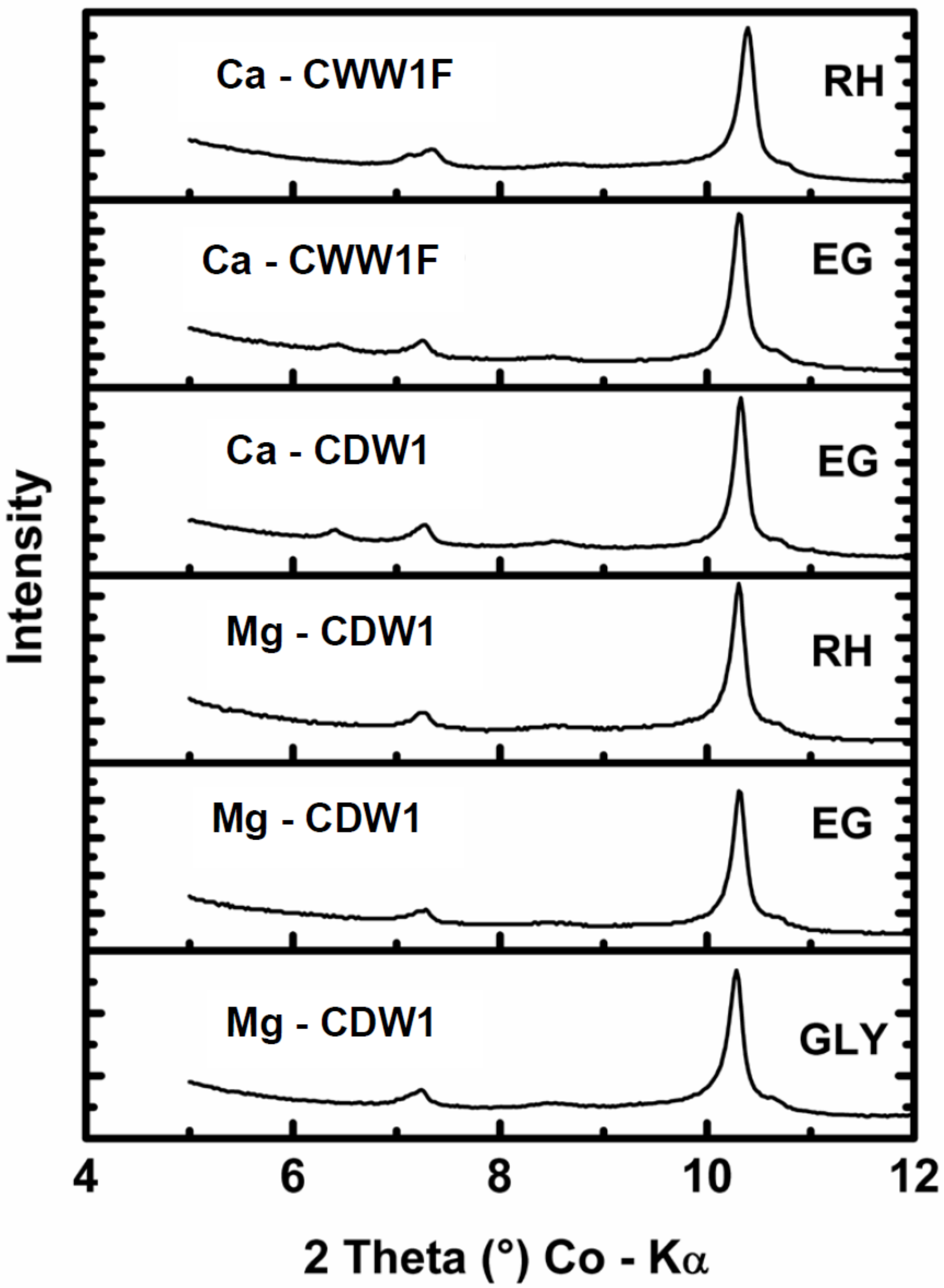


Figure 5.8: X-ray Diffraction Patterns of the Clay Minerals in Weathered Oil Sands Ore W1

5.3.4.2 Clay Quantification

The clay minerals and silt samples extracted by the Dean Stark apparatus was quantified by TOPAS^{TM} and the results are presented in Table 5.2. The corrensite, chlorite and lepidocrocite observed in the samples were not quantified since their diffraction peaks were not as intense as the other identified minerals. Table 5.2 gives the percent clay minerals present in the different ores W1, W2, W3, P and G. High fines ore P features the lowest kaolinitic to illitic mineral ratio, while low fines ore G has the highest kaolinitic to illitic mineral ratio. The kaolinitic to illitic mineral ratios of the weathered ores W1, W2 and W3 fall in between these two limits. It can also be observed that the weathered and high fines ores contain pyrite and siderite, which are absent in the low fines ore. The quartz content of the ores is as follows: G < weathered ores < P.

The mineral content of the silt samples given in Table 5.2 shows that the kaolinitic to illitic mineral ratio of the low fines ore G is the highest and high fines ore P is the lowest. It is interesting to see that weathered ore W3 has a very high fraction of siderite and pyrite when compared with the other oil sands ores.

The results in Table 5.2 also show that ore G has high percentage of kaolinitic minerals, which is the end product of a soil that has undergone weathering in the past, as soil development usually occurs through weathering[17]. The structure of kaolinite is rigid and non-expanding due to the presence of hydrogen bonding between building blocks. Hence, water and cations cannot occupy its interlayer

Table 5.2: Mineral Phases Present in the Isolated Solids from the Dean Stark Apparatus

Mineral Phase	Samples (wt. % Rietveld)									
	Clay Minerals					Silt				
	CDW1	CDW2	CDW3	CDG	CDP	SDW1	SDW2	SDW3	SDG	SDP
Siderite	2	1	5	0	< 0.5	1	< 0.5	14	0	1
Kaolinitic mineral	43	42	41	59	29	16	20	23	29	18
Illitic mineral	16	19	20	16	28	9	13	11	13	18
Quartz	29	29	26	16	35	67	61	45	44	57
Zircon	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Microcline	4	4	3	5	4	4	4	2	8	3
Rutile	1	1	< 0.5	1	1	1	1	1	1	1
Albite calcian	3	2	1	2	2	1	1	< 0.5	3	2
Pyrite	< 0.5	< 0.5	1	0	< 0.5	< 0.5	< 0.5	4	0	< 0.5
Anatase	1	1	2	2	1	1	1	1	1	1
Calcite	0	0	0	< 0.5	0	0	0	0	< 0.5	0
* K/I	2.61	2.20	2.03	3.59	1.04	1.70	1.57	2.11	2.16	1.02

* K/I means kaolinitic to illitic mineral ratio

space. As a result, the specific surface area of kaolinite is limited to its external surface, consequently limiting its cation exchange capacity. The high fines and weathered ores have a high illitic mineral content. Illite, though non-expanding, has a higher specifc surface area and cation exchange capacity than kaolinite.

In addition, ore W3 has high siderite content in comparison with the other ores. Siderite is a carbonate with a calcite structure[41]. It occurs in admixtures with clays, which is referred to as clay ironstone[41,42]. It can be formed by the substitution action of ferrous solutions on limestones. The Sci-Tech Encyclopedia[43] defined siderite as a mineral that can be found in near-surface sediments and ore deposits, which occurs in hydrothermal veins and sedimentary concretions formed in limestones and sandstones, and Precambrian banded iron formations that precipitated under acidic conditions. Siderite concretions consist of microcrystalline siderite which cements other detrital minerals and authigenic pyrite[44].

Table 5.3 presents the ratio of quantified clay minerals present in the aqueous phase to organic phase in both the bitumen froth and tailings. It can be observed that illite is more in the organic phase than aqueous phase of the bitumen froth and tailings of the ores with the exception of the low fines ore G. Siderite and illite –smectite are also more in the organic phase than aqueous phase of the bitumen froth and tailings of the ores with the exception of high fines ore P,

Table 5.3: Ratio of Minerals Present in the Aqueous Phase to Organic Phase

	Ratio of Minerals in Aqueous Phase to Organic Phase in Bitumen Froth					Ratio of Minerals in Aqueous Phase to Organic Phase in Tailings				
Mineral Phase	**CWW1F / COW1F**	**CWW2F / COW2F**	**CWW3F / COW3F**	**CWGF / COGF**	**CWPF / COPF**	**CWW1T / COW1T**	**CWW2T / COW2T**	**CWW3T / COW3T**	**CWGT / COGT**	**CWPT / COPT**
Siderite	0.2	0.2	0.2	0.2	0.8	NP	-	-	NP	-
K(90) - S	0.6	0.8	0.9	1.2	0.6	0.7	0.7	1.3	1.4	1.4
Kaolinite	1.1	0.9	1.0	0.7	0.7	1.2	1.2	0.7	1.0	1.1
I (85) - S	0.6	0.5	0.6	0.8	0.5	0.8	0.8	0.8	1.8	1.1
Illite	0.8	0.5	0.6	0.5	0.9	0.8	1.5	2.7	0.4	0.8
Quartz	2.7	2.1	1.9	1.8	3.7	1.7	0.9	1.0	0.8	0.9
Zircon	0.1	0.2	0.0	0.0	0.3	0.0	NP	1.8	0.6	0.7
Microline	1.0	1.2	1.7	1.1	1.6	0.5	0.8	1.0	0.9	1.0
Rutile	0.6	1.9	1.1	0.9	0.4	1.1	NP	0.5	0.5	0.5
Albite calcian	0.8	0.8	2.5	1.2	1.2	0.3	0.9	1.1	1.3	1.1
Pyrite	0.2	0.7	0.3	0.6	0.5	0.2	NP	NP	0.4	0.6
Anatase	0.4	1.4	1.6	1.1	0.6	0.6	0.6	0.9	0.5	1.1
Calcite	-	-	-	-	-	-	0.1	0.6	0.0	0.0

NP: Not Present , K-S: kaolinite-smectite, I-S: illite- smectite which has more illite-smectite in the aqueous phase than organic phase (for both bitumen froth and tailings).

A close examination of the kaolinitic minerals indicates an even distribution of kaolinite in the two phases, and sometimes the preference of kaolinite in the aqueous phase of the bitumen froth than in the organic phase with the exception of weathered ore W3. Ore W3 has more kaolinite in the organic phase than in the aqueous phase of the bitumen froth. The same observation was made for the minerals from the tailings with the exception of ores W2 and G having more kaolinite in the organic phase than tailings. Kaolinite-smectite is more in the organic phase than aqueous phase of the bitumen froth. This trend excludes ore P. A close look at the tailings shows more kaolinite-smectite in the aqueous phase for all the ores with the exception of ores W1 and W3 which possess more of this mineral in the organic phase.

As weathered ore W1 has the highest amount of organic coated solids (solids partitioned into the organic phase) and low fines ore G, the lowest. A comparison is made between the two ores of extremities. The minerals – kaolinite-smectite, illite, illite-smectite and siderite in the bitumen froth and tailings of weathered ore W1 are partitioned more in the organic phase than in the aqueous phase, while kaolinite is seen to be evenly distributed in both the organic and aqueous phase of this ore. In ore G, illite-smectite in both the bitumen froth and tailings seems to be the only clay mineral that is more in the organic phase than aqueous phase;

although the kaolinite-smectite and kaolinite in the bitumen froth and tailings were observed to be more in the organic phase than aqueous phase. These observations suggest that the smectitic minerals and illite have a preference for the organic phase than aqueous phase in ore W1. It is known that these minerals have a higher surface area and cation exchange capacity than kaolinite, which is evenly distributed in the aqueous and organic. The most common mineral that is more in the organic phase than in the aqueous phase in both weathered ore W3 and low fines ore G is illite-smectite.

5.3.5 Surface Area

The SA of the clay fraction of the isolated solids from the Dean Stark estimated from XRD and MB analyses are presented in Table 5.4. Only two samples – CDW1 and CDW2, were analyzed by MB to observe the accuracy of the SA determined from XRD patterns. It can be observed that the results from the two methods are within an error margin of 5 – 10 % of each other. Errors in the estimation of SA could be from clay quantification and peak deconvolution for XRD and homogeneous dispersion for the MB analysis.

The SA result shows that the low fines ore (G) has the lowest surface area and the high fines ore (P) has the highest. The SA for the weathered ores is between these two ores. Since illite has a higher surface area than kaolinite, this finding supports the XRD finding that shows the kaolinitic to illitic mineral ratio to be G > weathered ores > P.

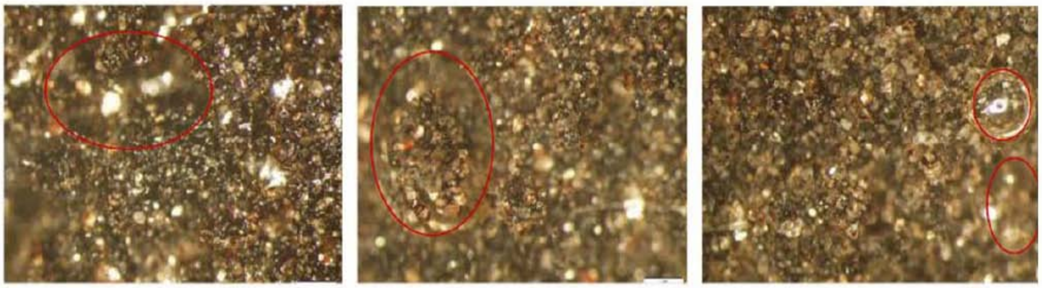
Table 5.4: Specific Surface Area of the Clay Minerals in the Different Oil Sand Ores

Samples	Specific Surface Area (m^2/g)	
	X-ray Diffraction	Methylene Blue
CDW1	77	74
CDW2	81	89
CDW3	98	ND
CDG	66	ND
CDP	107	ND

ND: Not Determined

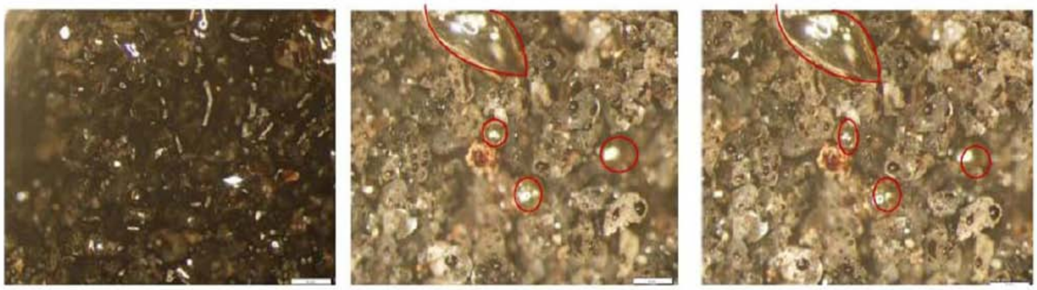
5.3.6 Bitumen Liberation Result

The bitumen liberation results of ores W1, W3 and G are presented in Figure 5.9. This test was performed on ore W3 and G due to their similarities in PSD and clay content. W1 was analyzed because of the high carryover of solids into the bitumen froth and low bitumen recovery with the selective occurrence of corrensite in CWW1F. During the analysis of ore W1, a high amount of aggregated solid particles containing a small amount of bitumen are observed to attach to air bubbles (at 20, 150 and 550 seconds) that were entrained within the oil sands ore. The carry-over of solids into the bitumen froth by attachment onto air bubbles supports the result of high froth solids content obtained from solids partitioning tests. The poor processability of ore W1 could be explained by its high organic coated solids content when compared with the other ores and fines content when compared with the other weathered ores.



W1 (20 seconds) W1 (150 seconds) W1 (550 seconds)

W3 (20 seconds) W3 (150 seconds) W3 (600 seconds)



G (20 seconds) G (150 seconds) G (200 seconds)

Figure 5.9: Images of the Bitumen Liberation Tests in Ores W1, W3 and G (Air Bubbles Outlined in Red)

Bitumen droplets were observed to rapidly and effortlessly recede (within 200 seconds) in low fines ore G. The opposite occurred with weathered ore W3, which has the same PSD as that of ore G. In ore W3, there is a preference for the bitumen to spread on and be trapped within the sand grains rather than to recede into bitumen droplets. Hence, bitumen droplets formed at a very slow rate (at 600 seconds) on ore W3 – the slowest for all the ores analyzed. We can recall that when compared with the other oil sands ore, ore W3 contains the highest amount of divalent cations – Ca^{2+} and Mg^{2+}, and minerals pyrite and siderite. Moreover, ore W3 possess more organic coated solids and a lower kaolinitic to illitic mineral ratio (higher surface area) than ore G. These factors contribute to the slow liberation of the bitumen from the sand grains in ore W3. Even though the solids in ore W3 are of the same PSD and clay content as in low fines ore G, in which bitumen recession has been rapid.

The role of divalent cations in oil sands processability has been explored in previous communications[6, 45]. Sanford[6] reported that these cations could interact with anionic surfactants by converting mono-valent metal soaps to multi-valent metal soaps, thereby making them less active. The divalent cations could also act as bridging agents between clays and other species. The presence of a higher amount of illitic minerals in W3 than in G, would also promote the interactions between these divalent cations and other species. The concretion property of siderite could induce a cementation effect on oil sands, which may have a limiting effect on the liberation of bitumen. This is probably accurate as the weathered oil sands W3 was observed to be difficult to break into smaller pieces unlike the other ores. Hence, a high input of mechanical energy is required in order to liberate the bitumen from the oil sand grains.

5.4 Summary

The effect of weathering on the processability of oil sands includes a high carryover of solids into the bitumen froth and slow bitumen liberation from the sand matrix of the oil sands. These eventually lead to the low recovery of bitumen from oil sands. This study shows that weathered ores is characterized by the presence of certain minerals such as corrensite, siderite and pyrite as well as a low kaolinitic to illitic mineral ratio in comparison to an unweathered low fines oil sands ore. The occurrence of a high amount of divalent cations and organic-wet solids in weathered ores was also reconfirmed. The presence of these materials contributes to the low processability of weathered ores in different ways. These include the interaction of divalent cations with illite and other species in the oil sands, and the cementation effect of the siderite concretions on the oil sand grains. Illite-smectite was found to be partitioned in the organic phase of the oil sands when compared with those from the aqueous phase. In addition, corrensite – a mixed-layer clay, was identified for the first time in oil sands. The role of this clay in the processability of oil sands ores remains unknown.

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CHAPTER SIX

CONCLUSIONS

6.1 Overall Conclusions

The overall conclusions from the study on solids extracted from different oil sands are presented below.

1. Prior to characterizing the organic coated solids isolated from the different oil sands ores, it was crucial to develop an effective method to remove organic matter (OM) from the clay minerals without changing the characteristics of mineral phases. An investigation was conducted to determine an effective method for accomplishing this objective. The results of infrared spectra, x-ray diffraction (XRD), elemental analysis, and wettability tests showed that low temperature ashing (LTA) and chemical treatment by hydrogen peroxide (H_2O_2) were effective in the removal of OM. Upon H_2O_2 or LTA treatment, the IR bands at 2926cm^{-1} and 2854 cm^{-1}, corresponding to $–CH_2–$ and $–CH_3$ stretching vibrations disappeared, indicating the removal of OM. The removal of OM resulted in a significant reduction in the amounts of carbon, hydrogen and nitrogen present on the treated clay sized minerals (CSM), thus making the treated particles hydrophilic.

   Compared with H_2O_2 treatment, removal of OM by LTA is preferred because it does not change the mineral phases of inorganic matter. In the case of H_2O_2 treatment, siderite was found to be oxidized as indicated by the results of infrared spectra, XRD analysis and cation exchange capacity (CEC) determination. This study clearly shows that LTA is a better choice in OM removal from CSM isolated from oil sands, and its usage ensures more accurate characterization of original mineral solids phases than the widely used H_2O_2 treatment.

2. Organic coated solids isolated from the bitumen froth of the different ores were observed to possess more clay minerals and to be more associated with carbonates, transition metals and probably oxides and hydrous oxides of iron and aluminum, as implied by the infrared spectra and confirmed by XRD, energy dispersive x–ray spectroscopy (EDX) and elemental analysis. This association with carbonates could be due to the similarity between carbonate anions and carboxyl groups as explained by Carter et al.[+]

   Moreover, most of the quartz minerals were observed to preferentially distribute in the tailings than in the bitumen froth. More organic coated solids were found in the weathered oil sands than in the other types of oil sand ores. The presence of organic coated solids is observed to reduce bitumen recovery from oil sands.

[+] Carter, W. P.; Mitterer, R. M. *Geochim. Cosmochim. Acta*. **1978**, *42*, pp 1231-1238.

3. A study of weathered oil sands ores indicates that the effect of weathering on the processability of oil sands include a high carryover of hydrophilic solids into the bitumen froth and slow bitumen liberation from the sand matrix of the oil sands, which eventually leads to low bitumen recovery. This study shows that weathered ores are characterized by the presence of certain minerals such as corrensite, siderite and pyrite as well as a low kaolinitic to illitic mineral ratio in comparison to an unweathered low fines oil sands ore. The occurrence of a high amount of divalent cations and organic-wet solids in this type of ore was also confirmed. In addition to the effect of wettabiltiy on ore processability, the presence of these materials contributes to the low processability of weathered ores in different ways. These include the interaction of divalent cations with illite and other species in the oil sands, and the cementation effect of the siderite concretions on the oil sand grains. Illite-smectite was found to be preferentially partitioned in the organic phase of the oil sands. In addition, corrensite – a mixed-layer clay, was identified for the first time in oil sands. The role of this clay in the processability of oil sands ores remains unknown.

6.2 Contribution to Original Knowledge

The following contributions were made to original knowledge of oil sands research.

1. The use of low temperature ashing as opposed to chemical treatment such as hydrogen peroxide was established as a preferred method to remove adsorbed organics on clay sized minerals.

2. A distinction in mineralogy of weathered ores as compared to some low- and high-fines content ores was determined. Siderite, pyrite and a low kaolinitic to illitic mineral ratio are the norm for weathered ores when compared with low fines oil sands ores.

3. In addition to the mixed-layer clay minerals – illite-smectite and kaolinite-smectite previously documented in oil sands ores, high charged corrensite (chlorite-vermiculite mixed-layer clay) was identified in one of the weathered ores that was studied.

4. An improved understanding of organo-mineral interactions in oil sands ores was achieved as organic matter was observed to be linked with carbonates in solids isolated from the bitumen froth.

5. The preferential partitioning of illite-smectite in the organic phase during oil sands extraction was established.

6. Overall, water and a mixture of heptane and toluene at a 2:1 volume ratio can be successfully used to partition the solids in the bitumen froth and

tailings after a warm water extraction by the Denver flotation method and study their characteristics.

6.3 Suggestion for Future Work

In this study, corrensite (mixed-layer chlorite-vermiculite) was identified in one of the samples that were investigated. This mixed-layer clay has never being documented in connection with oil sands. It would be expedient to study the implication of this clay in processing oil sands.

Furthremore, it would be worthwhile to study the adsorption mechanism of organic matter on minerals (clays and carbonates). This could be done by developing a simple model system of organic compounds and performing adsorption experiments in the presence of clays and carbonates. This experiment would provide insights into the swelling characteristics of the clays with respect to the insertion of different cationic ions and organic matter as well as the types of metal ions and the nature of organic matter that contribute to organo-mineral complexation.

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