University of Alberta

OIL SANDS WEATHERING

by

©

Yong Gu

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

Department of Chemical and Materials Engineering

Edmonton, Alberta

Fall, 2006

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ISBN: 978-0-494-22274-4
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Abstract

Oil sands weathering has been studied by artificially treating oil sands samples under controlled environment. The objective of this study is to identify the possible reasons for the oil sand weathering and to determine its effect on the processability of the weathered ores.

The effect of water-loss on oil sands weathering is investigated by treating the sample inside an oven to different levels of remaining connate water. The results show that the recovery decreases and the froth quality deteriorates when the remaining water content in the treated ore samples decreases. The samples are also treated in air and nitrogen environments. By comparison, it is found that the oxidation plays a role in oil sands weathering.

The hydrophobicity of solids in the treated oil sands ores is examined for all the treatment conditions. From the photographs taken for this study, it is clear that the hydrophobicity of solids changes with remaining water content of the treated samples. This finding is confirmed by quantitative analysis of solids hydrophobicity.

Through this study, it is also found that the effect of the weathering on processability is, to some degree, reversible and the treatment process has no impact on the contact angle of bitumen and the surface tension of tailings water. No correlation is found in this study for the tailings water chemistry with various treatments.

Acknowledgement

I would like to express my sincere gratitude and appreciation to:

- My supervisor Professor Jacob Masliyah, NSERC Industrial Research Chair in Oil Sands Engineering and Canada Senior Research Chair, for his excellent guidance, immense encouragement and patience throughout my study.
- Professor Zhenghe Xu, NSERC/EPCOR/AERI Industrial Research Chair in Advanced Coal Cleaning and Combustion Technology, for his wonderful suggestions and generous help.
- Dr. Randy Mikula, for his invaluable discussion.
- Technician Mr. Jim Skwarok for his generous help.

Syncrude Canada Ltd is gratefully acknowledged for providing the oil sands and process water used for this study.

I would like to thank all the members of oil sands research group for their help and NSERC Industrial Research in Oil Sands for financial support.

I would particularly like to thank my family, especially my wife Jing Xie and my daughter Helen Jingyi Gu for their love, support and understanding.

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Chapter 1: Introduction

1.1 General

Oil sands containing valuable fossil fuel in the form of bitumen, are also known as tar sand or bituminous sands. Bitumen is best described as a thick, sticky form of crude oil. At room temperature, it is much like cold molasses. Oil sands deposits are one of the world's largest oil resources. They are found all over the world, usually in the same geographical location as conventional petroleum. Alberta's oil sands comprise one of the world's two largest sources of bitumen (the other is in Venezuela), occurring in three locations: the Athabasca, Peace River and Cold Lake regions, which cover 141,000 square kilometres. The largest deposit is the Athabasca deposit (Camp, 1976 and 1977; Masliyah et al. 2004).

The fossil fuel in Alberta's oil sands reserve is larger than Saudi Arabia's oil reserve. In Alberta, the total estimate of bitumen in-place is 1.7 to 2.5 trillion barrels of oil. In the Athabasca deposit, there are 830 billion barrels (Outrim and Evans, 1997; Morgan, 2001; Masliyah et al., 2004). Figure 1-1 shows the status of the world oil reserves. Alberta's oil sands typically contain 10% bitumen, 4% water, and 85% quartz with some fine clays.

Due to high oil prices in recent years, huge investments have been injected into the oil sand processing industry, which has made the oil sand industry one of the fastest growing industries in Canada. It is expected that the total bitumen production will reach 1,600,000 barrels per day by 2015, which is well over 50% of the total Canadian daily oil production. With the continual decline of conventional oil reserves, oil sand deposits will continue to become increasingly significant in Canada's overall energy scenario (FTFC, 1995,vol.I).

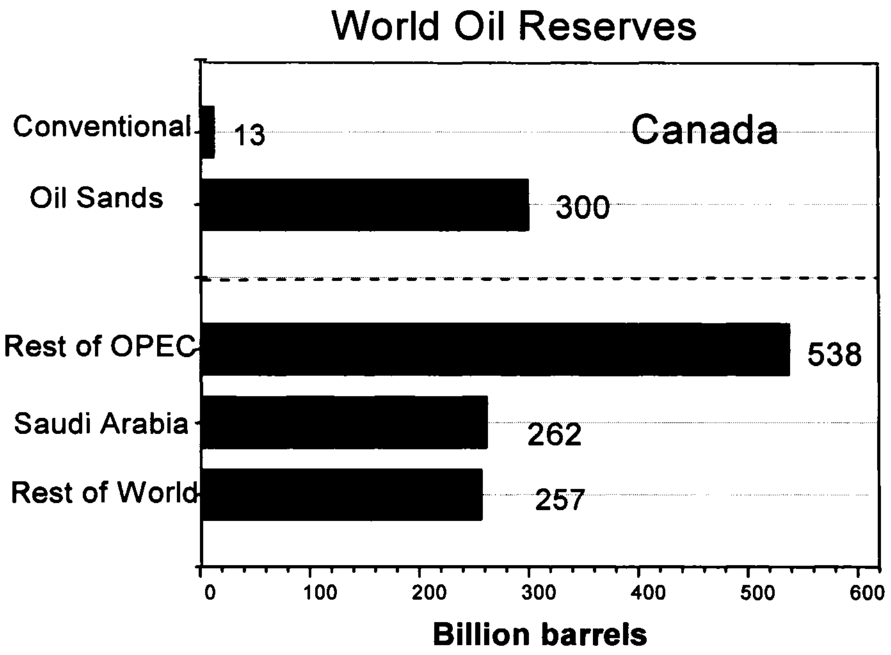

Figure 1-1: World proven oil reserves. (Masliyah, 2004)

1.2 Bitumen Production

Since the first European explorers discovered the Athabasca oil sands, extensive efforts have been made towards achieving economic development for this energy resource. In early twenties of the last century, Dr. Karl Clark and his colleagues developed a hot water extraction process to separate the bitumen from the sand. This process is the foundation of current processing technology for surface mined oil sands. Due to the pioneering work of Clark, bitumen extraction from oil sands was founded on a scientific basis and oil sands became a very important energy resource in Canada.

The processing of oil sand involves three parts: An open pit mine, a hot water extraction plant to recover bitumen from the oil sands and an upgrading complex to upgrade the extracted bitumen to a light synthetic crude (Morgan, 2001; Masliyah, 2004), which can be further processed in refineries. The basic steps of bitumen recovery comprise: bitumen liberation from the sand grains, bitumen-bitumen coalescence and aeration of liberated bitumen to air bubbles, and separation of liberated and aerated bitumen aggregates from the water-solid slurry (bitumen-air bubble aggregates float to the top of the slurry and form bitumen froth). The bitumen froth product is sent to froth treatment. Usually naphtha is used to reduce the bitumen viscosity and the centrifuges are used to remove the solids and water. After recycling the diluents, the final bitumen is further upgraded into light synthetic crude. Figure 1-2 shows a generalized scheme for oil sand processing.

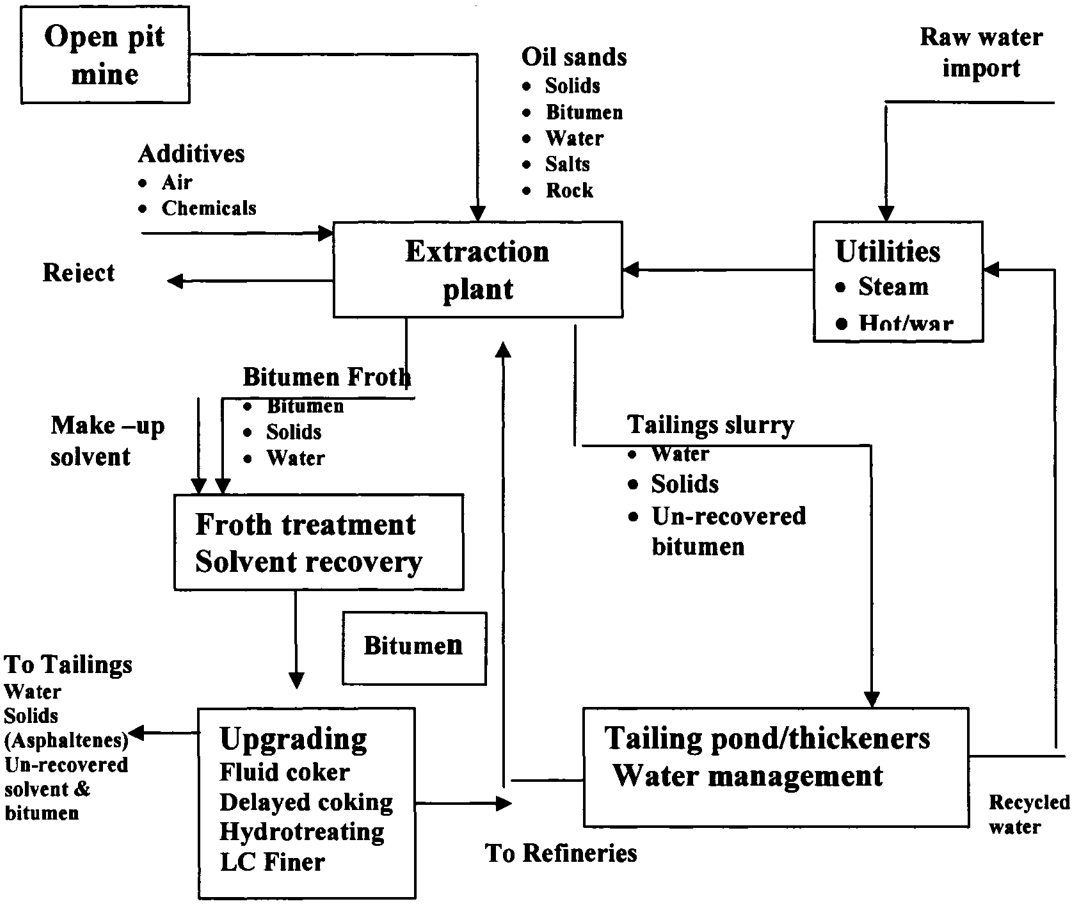

Figure 1-2: Generalized scheme for oil sand processing (Masliyah, 2004)

The operating temperature plays a major role in oil sand processing and the design of a bitumen extraction plant. The decision on an appropriate operating temperature involves the residence time of oil sand lumps in the extraction unit, the unit operations within the extraction plant, availability of excess energy, and so on (Masliyah et al, 2004). Suncor and Syncrude started their bitumen extraction operations using the Clark Hot Water Extraction (CHWE) process operating at 70-80°C. High operating temperatures cause high energy consumption, increasing the cost of bitumen production. Now, both Suncor Steepbank and Syncrude North Mines operate at about 50°C, while Syncrude Aurora plant operates at about 35°C.

The CHWE technology demonstrated huge success in a number of commercial operations. The recovery of bitumen easily exceeded 93% for a good processing ore. Despite this success, there are a lot of technical challenges, in particular to treat so-called "weathered ore".

1.3 Oil sand weathering

From the very first extraction tests, it was observed that oil sands which was freshly mined could be processed far better than the one was left sitting for weeks. Anyone who had experimented with the recovery of bitumen by the CHWE process had found the oil sand's deterioration after it was removed from the deposit. The processability of oil sands varied with time that the sample had been stored. We call this phenomenon "oil sands weathering". By storing large samples in fully sealed containers at temperature as low as possible, weathering was slowed down, but could never be stopped .

What happens to oil sands ores during storage is not well understood. However, there are several mechanisms that have been proposed. The explanations of such processability change are: dehydration, bacterial activity and oxidation of bitumen and contained minerals, such as pyrite.

There are also freshly mined oil sands that appear to have undergone in situ weathering that mimics the effects of storing mined oil sands.

1.4 Objective

The objectives of this thesis are to study the mechanisms of oil sands weathering and the reversibility of the weathering process. Oil sands are treated inside an oven to control the weathering process. Hot-water extraction technology is used to extract bitumen from treated oil sands samples. More specific objectives are:

- To investigate the effect of water-loss during oil sands weathering so that we can understand how the recovery and froth quality of bitumen change with water content of the treated oil sands samples.
- To study the effect of oxidation during oil sands weathering by treating oil sands samples with nitrogen on ore processability of the weathered ores. This allows us to investigate the differences between air treatment and nitrogen treatment.
- To observe the hydrophobicity change of oil sands solids, after air treatment and nitrogen treatment. The hydrophobicity of solids is analyzed quantitatively using the procedure developed from this thesis research.
- To analyze the tailing water chemistry and to measure the surface tension of the tailing water before and after treatments.
- To investigate the reversibility of the oil sands weathering process using the procedure developed from this thesis research.

1.5 Organization of the thesis

This thesis is organized in the following way:

Chapter 1: The oil sands and bitumen production, as well as the oil sand weathering phenomenon are briefly introduced. The objectives of this study and the overview of this thesis are also given in this chapter.

Chapter 2: A review of the fundamentals of oil sands and bitumen extraction, including the composition, the physical properties and microstructure of the oil sands; and the extraction technology and some factors which impact the oil sand processing. The state of research on oil sands weathering is reviewed.

Chapter 3: A detailed description of experimental systems and procedures.

Chapter 4: Characterization of the oil sands samples used for this study, including the composition and size distribution of solids extracted from the sample. Fines content is determined. More importantly, weathering has been examined by both natural weathering and artificial weathering.

Chapter 5: All the results, findings and discussion are given in this chapter.

Chapter 6: A summary of conclusion from this study is given in this chapter.

Chapter 2: Literature Review

2.1 The characteristics of Athabasca oil sands

2.1.1 Oil sands composition

Oil sands are a mixture of bitumen, connate water and solids as well as some electrolytes. The amount of bitumen in the oil sands ranges from 0 – 16% by weight. Although the bitumen content in the oil sands varies, the total content of bitumen and its connate water is fairly constant with a value of about 16%. The balance of 84% is the mineral solids. Usually, oil sands is classified according to its bitumen content: an ore with bitumen content of 6-8% is considered a poor ore, a content of 8-10% is considered an average grade, and an ore with a bitumen content above 10% is considered a rich ore.

The chemical composition of bitumen is extremely complex. It is almost impossible to analyze the structures of all the components in bitumen. For the elemental composition of bitumen, it contains mainly carbon, hydrogen, sulphur, nitrogen, oxygen and metals present in organic structures. Table 2-1 shows some chemical analysis of bitumen for the Athabasca oil sands (Nelson and Gray, 2004). Bitumen is often classified into four classes:

- Coke and solids: Insoluble in tetrahydrofuran (THF)
- Preasphaltenes: Soluble in THF, but insoluble in benezene
- Asphaltenes: Soluble in benezene, but insoluble in n-pentane
- Maltenes: Soluble in n-pentane

The maltenes fraction can be further separated into the following fractions: saturates, aromatics and resins.

Table 2-1 Typical Composition of Athabasca Bitumen

Bitumen	C (wt. %)	H (wt. %)	N (wt. %)	O (wt. %)	S (wt. %)	Ni (ppm)	V (ppm)
Syncrude	83.1	10.6	0.4	1.1	4.8	150	290
Suncor	83.9	10.5	0.4	1.0	4.2		

The connate water in the oil sands is quite similar to seawater, containing various amounts of organic and/or inorganic ions, such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^{-1}, or -COOH. The amount of ions present in the connate water varies over a wide range. Salt content is high in a poor ore, but low in a rich ore.

The mineral composition of the solids is of over 90% quartz with minor amounts of potash, feldspar, chert and muscovite (Carrigy and Kramers, 1973; Boon, 1978; Masliyah, 2004). Quartz is the most abundant. Clay only appears in the fines (<44μm) fraction and is mainly kaolinite and illite with a small amount of montmorillonite. Heavy minerals are also present in the solids of oil sands. The total solid analysis is shown in Table 2-2.

Table 2-2, Mineral components in total oil sands solids (Hepler and Smith, 1994; Masliyah el al., 2004)

Component	Weight, %
Quartz	82
K - feldspar	5
Calcite	Trace
Dolomite	Nil
Siderite	Trace
Pyrite	Nil
Kaolinite	4
Illite	7
Chlorite	1
Smectite	Trace
Mixed layer clays	1
Anhydrite	Trace

2.1.2 Microstructure of oil sands

The successful application of water-based technology to recover bitumen from Athabasca oil sands lies in the key fact that the sands grains in the oil sands are hydrophilic. Even more, there is a notion that a thin layer of water surrounds individual sand grains, separating them from the bitumen (Masliyah et al., 2004). It was hypothesized (Fitzgerald, 1978) that if the intervention of the water layer were not present, the process of bitumen separation from oil sands would not only be difficult but also not be economically feasible. However, the existence of such a water film remains to be directly verified experimentally.

Long before the commencement of the first commercial operation of bitumen extraction, even from the early stage of oil sand development, Clark had postulated the presence of a water film around the sand grains (Clark and Pasternack, 1932; Masliyah, 2004). In 1967, Cottrell first proposed a structural model for oil sands in terms of the interactions between water, bitumen and mineral particles. Cottrell assumed that a water film of uniform thickness surrounded the sand grains, while clay minerals were suspended in the water film layer. The water film was encased by bitumen, which filled the voids between the individual sand grains (Takamura, 1982). Mossop updated the model in 1980. In this refined model, the quartz grains were all in direct contact with each other, and they constituted a stable framework that remained virtually unchanged when the fluids were mobilized. The water film around the grains, only a few micrometer thick, formed a physically continuous sheath that prevented direct contact between bitumen and quartz. The bitumen phase was also continuous, linked from one pore to the next through a three-dimensional network of pore throats. Clay minerals were attached to the surface of sand grain, and it was unlikely that they protruded through the water envelope (Mossop, 1980). Mossop believed that the presence of the water film made the hot water process possible. The schematic models of Cottrell and Mossop are shown in Figure 2-1.

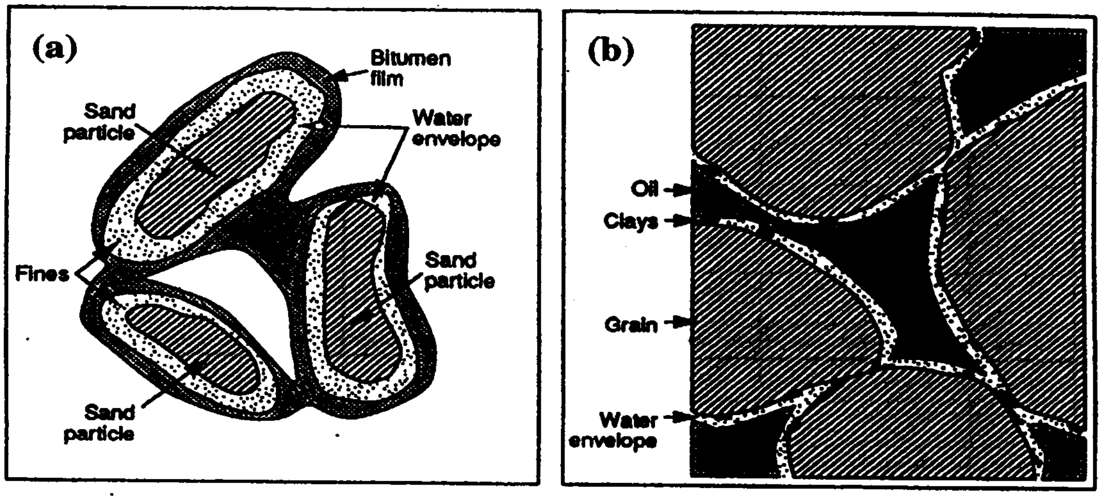

Figure 2-1: Schematic models of oil sands: (a) Cottrell and (b) Mossop

Although the above models have been widely accepted, they have certain limitations: the models assumed that the thickness of the water film was uniform, and the models are only applicable to high-grade oil sand.

Takamura developed a more refined model in 1982. In this model, the water in the oil sands appeared in three forms: as pendular rings at grain-to-grain contact point, as a roughly 10nm thick film which covered the sand surfaces, and as water retained in fine particle clusters. The sand grains occupied roughly 65 percent of the pore volume. In the case of high-grade oil sands, between 10 and 15 percent of the pore volume was filled with water with the rest of the space being occupied by bitumen. For the sand grain surface, 30% of it was covered by the pendular water rings, and 70% of it was covered by a thin water film. This water layer was stable because of the double layer repulsive forces acting between the sand and the bitumen surfaces. The thin water film would also cover the clay minerals in the oil sands. In the case of low-grade oil sands, clusters of fine particles (<44μm) existed between the coarse sand grains. These fines are saturated with water. Thus the amount of connate water in oil sands increased linearly with increasing fines contents. Figure 2-2 shows the refined structural model of oil sands (Takamura, 1982).

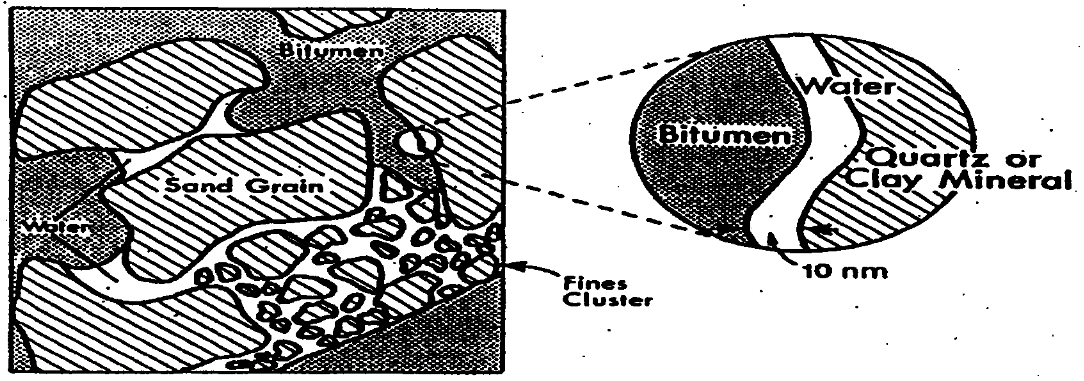

Figure2-2: The refined model of the structure of Athabasca oil sands structure.

2.1.3 Some physical properties

(I) Bitumen viscosity

Viscosity is a physical property of a fluid that offers resistance to flow. The viscosity of bitumen affects many aspects in oil sands extraction; for example, the size reduction of oil sand lump, bitumen liberation from sand grains, and bitumen aeration. Bitumen viscosity varies tremendously depending on geographical location and depth of sampling. Hupka et al. (1983) studied the importance of bitumen viscosity in oil sands extraction and found that the bitumen viscosity varied significantly depending on the types of the ores. The viscosity of bitumen was high for the oil sands with low bitumen content and it was low for the ores with high bitumen content. In all the cases studied, separation efficiency could be correlated with bitumen viscosity and optimized by viscosity control. Adjustment of the bitumen viscosity to below 1.5 Pa·s was found to be optimum for the hot water processing technology.

In order to obtain reliable viscosity data of bitumen, great care is needed because the bitumen viscosity is very high. The difficulty in the measurement of bitumen viscosity is that: the conclusion could be easily falsely made that the bitumen is a shear thinning liquid. In fact, bitumen behaves as a Newtonian fluid where the applied force is proportional to the induced shear rate. The reason for this mistake is quite simple: the heat generated within the bitumen sample due to viscous dissipation during the measurement, is ignored. In the case where "bob" is used to measure the bitumen viscosity, which is quite typical rheology measurement device, the inner cylinder is rotated. This rotation generates heat because of viscous dissipation inside the bitumen fluid. Although the cup is maintained at a constant temperature by circulating water, the temperature of bitumen inside the gap is higher than the temperature of circulating water. Since bitumen viscosity is very sensitive to temperature, erroneous viscosity data could be generated if special attention is not paid to the bitumen heating by viscous dissipation.

The viscosity of natural bitumen can be reduced dramatically by blending with light distillates such as naphtha, pure organic solvents, or high-pressure light gases (Seyer and Gyte, 1989). Dilution with naphtha is important to a number of processes. Dissolved gases have limited potential for viscosity reduction because of the limits to their solubility in bitumen at a given temperature and pressure.

(II) Bitumen density

Although there are large differences in the measured densities of bitumen, for Athabasca oil sands, the density ranges from 0.99 g/cm^3 to 1.06 g/cm^3. Bitumen density is very close to the density of water, and decreases with increasing temperature. Figure 2-3 compares densities of bitumen and water as a function of temperature.

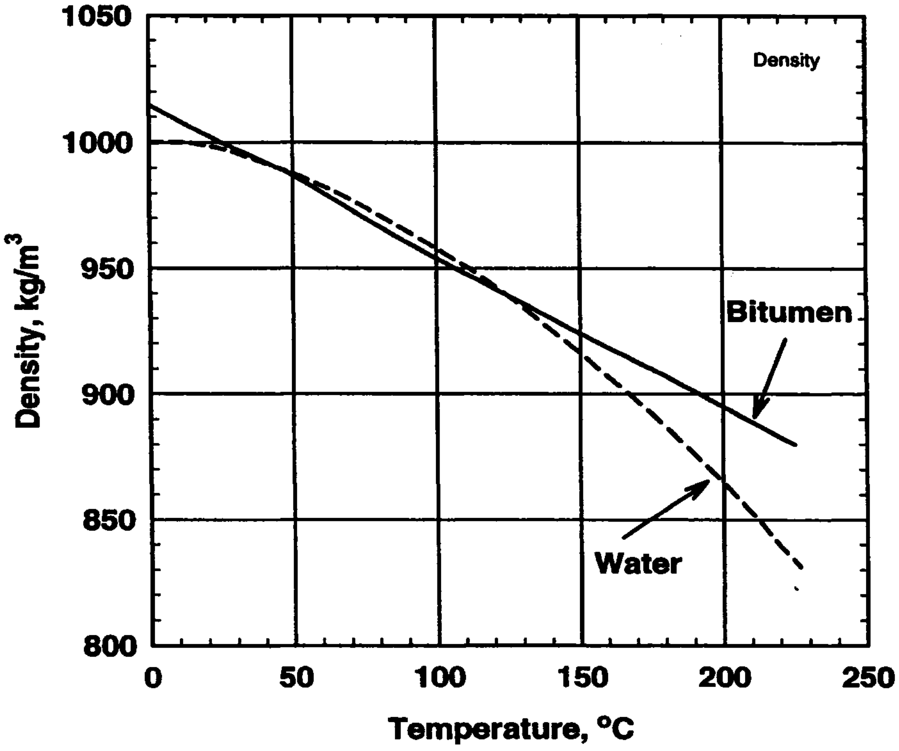

Figure2-3: Density comparison between bitumen and water (Takamura and Issacs, 1989; Masliyah et al, 2004)

Due to the very small difference in density between bitumen and water within the extraction temperature range, air attachment is extremely important for bitumen recovery by flotation, which depends on the density difference (Masliyah et al, 2004).

2.2 Oil Sands Extraction Fundamentals

2.2.1 Water-based technology of oil sands extraction

Since K. A. Clark developed the hot-water extraction technology for oil sands extraction in Alberta, many processes had been commercialized. Syncrude, one of the largest oil sand processing companies, started its first operation in 1979, followed by Suncor and Albian Sands. The bitumen recovery usually involves following several steps (Masliyah et al, 2004):

(1) Mining of oil sands

Commonly, it is open-pit mining. Shovels and trucks are used to remove the overburdens, which are on the top of oil sands deposit, and to load the oil sands. The mined ore is transported to the extraction plant.

(2) Oil sands ore preparation

Crushers are used in this stage to reduce the size of oil sands lumps. Mixing boxes, stirred tanks, cyclo-feeders or rotary breakers are used to mix oil sands with water. Chemical additives can be added at this stage.

(3) Digestion of oil sand lumps with subsequent bitumen liberation and aeration

Tumblers and slurry hydrotransport pipelines are used for bitumen liberation from the sand grains, bitumen-bitumen coalescence and aeration. Hot water, steam and caustic soda (NaOH) are added to the oil sands while the tumblers rotate. In 2003, the tumblers at Suncor were retired and only three tumblers are in use at Syncrude. Small amounts of air can be added to the hydrotransport pipelines to allow for more efficient bitumen aeration.

(4) Separation of the liberated bitumen from the water-solids slurry by flotation

Large gravity separation vessels are used for primary separation. The coarse sands settle to the bottom of the separation vessel and are removed as the "tailings stream". A portion of the slurry from the central part of the vessel is removed as the "middlings", and the bitumen froth floats to the top of the vessels.

Flotation cells are used for further recovery of bitumen, including the bitumen droplets from the middlings that did not float to the top of the gravity separation vessels, and from the tailings oil recovery vessel, cyclo-separators or hydrocyclones.

(5) Froth treatment

After being "cleaned" in stirred tanks to remove some of water and solids, the aerated bitumen from the gravity separation vessels and flotation cells are de-aerated in towers. The de-aerated bitumen is processed in the froth treatment plant to remove as much as possible of the contained minerals and water. In order to reduce the viscosity of the bitumen froth, both Syncrude and Suncor use naphtha while Albian uses paraffinic diluents to dilute the froth. Inclined plate settlers, cyclones, centrifuges and thickeners are used to remove the solids and water from bitumen froth.

(6) Fine tailings management

Syncrude and Suncor employ consolidated (composite) tailing (CT) processes to consolidate the fines and capture the coarse particles by adding gypsum together with mature fine tails. Fine and coarse solids become a non-segregating mixture, thereby releasing the contained water for further use in the extraction process. At Albian Sands, the tailings are treated by the cyclone first. The coarse tailings from the cyclone underflow are pumped to the tailings pond. The fine tailings from the cyclone overflow are treated with flocculants before being thickened in a thickener and pumped into the tailings pond. All the three oil sands operators are currently planning to use paste technology for immediate water release and recycle for bitumen processing.

A typical bitumen extraction flowsheet (Masliyah et al, 2004) is shown in Figure 2-4.

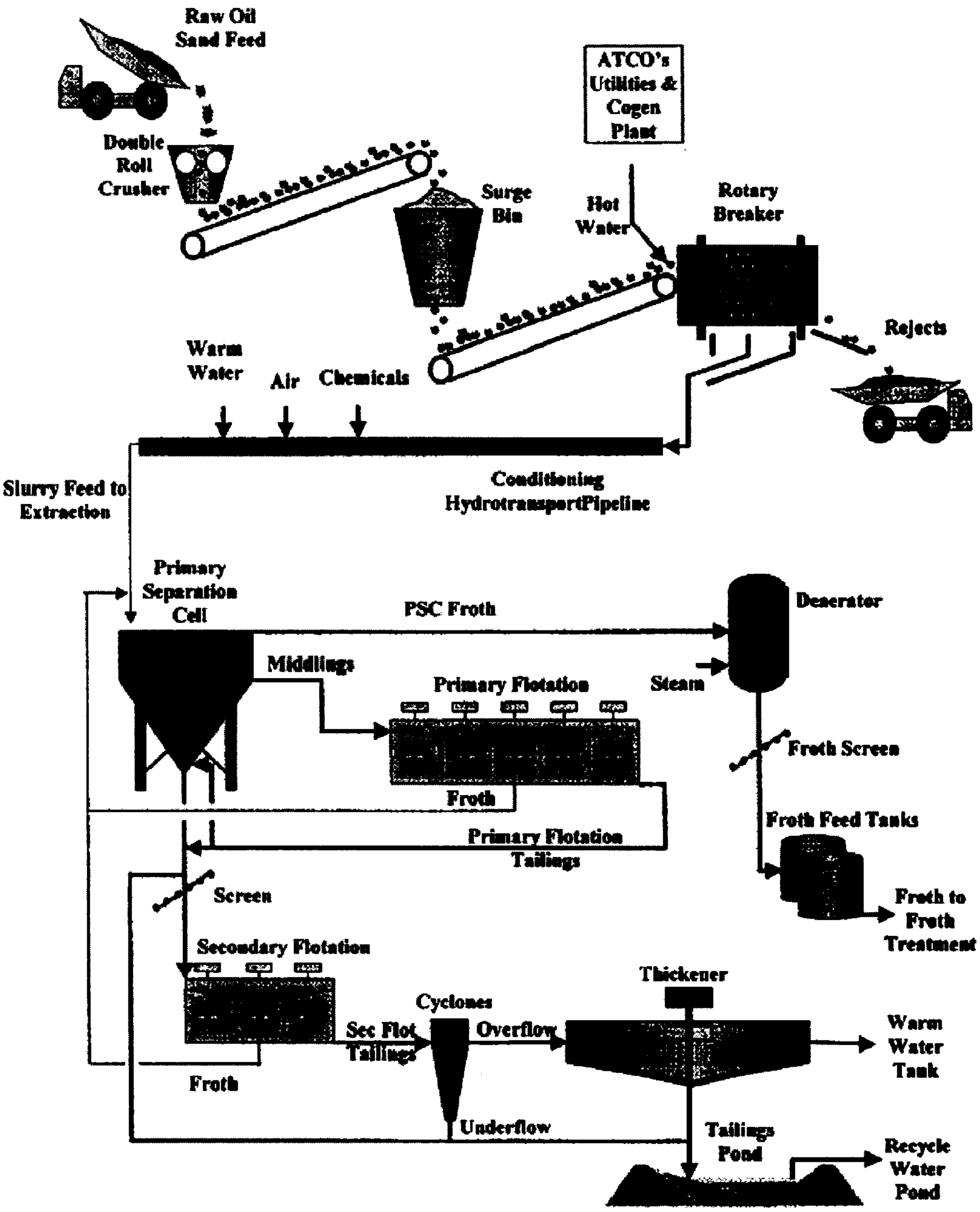

Figure2-4: A typical bitumen extraction flowsheet: ore preparation, slurry conditioning, extraction and tailing management. (Courtesy of Robert Tipman, Shell Canada Lt; Masliyah et al., 2004)

2.2.2 Ablation of oilsands lump and liberation of bitumen

Takamura et al. proposed a mechanism for initiation of bitumen displacement from oil sand as shown in Figure 2-5. Two sand grains represent an oil sand aggregate and the thin aqueous film on the sand surface was omitted from the graph because of its microscopic dimension [Figure 2-5 (a)]. When the aggregate was immersed in water, bitumen would recede from sand grain surfaces, moving to the grain-to-grain contact point and forming a drop of toroidal shape [Figure 2-5 (b)] that is thermodynamically more stable. When the bitumen started to migrate to the grain-to-grain contact point, it also led to the thinning of the local bitumen film [Figure 2-5 (c)]. Finally the bitumen film ruptured and the water film between the bitumen and the solid grains would mix with aqueous phase.

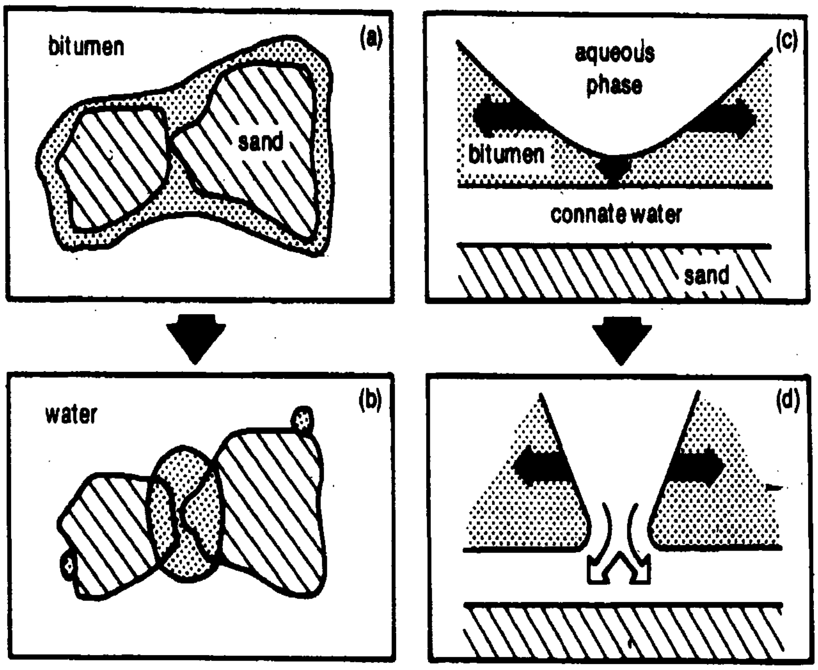

Figure2-5: Schematic diagram showing the initiation of bitumen displacement (K. Takamura and R. Chow 1983)

For the size reduction of an oil sand lump and the liberation of bitumen from individual sand grains to form free bitumen aggregates, Masliyah et al. (2004) proposed the following conceptual steps:

(1) Oil sand lump size reduction

When the oil sands lumps were mixed with hot water inside a tumbler, rotary breakers or hydrotransport pipeline, their outer layer would be heated. The viscosity of bitumen would decrease. Under the action of mechanical shear, the outer layer could be easily sheared away and a fresh lump surface would be exposed to the environment. The process schematically shown in Figures 2-6 and 2-7 would repeat itself until oil sand was ablated.

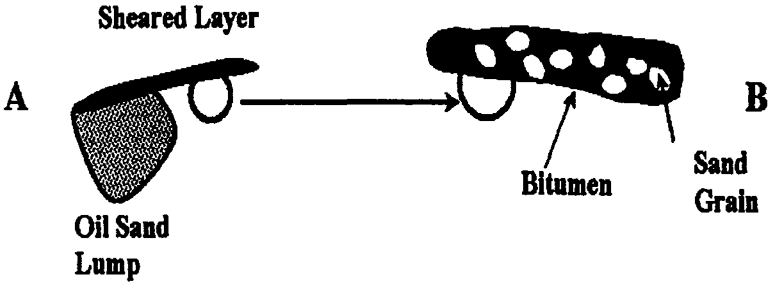

Figure2-6 (A) Ablation of an oil sand lump, (B) A sheared layer of oil sand

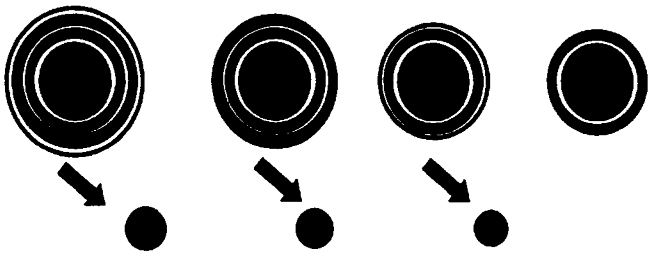

Figure2-7: A model form of lump ablation (Masliyah, 2004)

(2) Formation of the three-phase contact point

After the ablation of an oil sands lump, for bitumen to liberate from sand grains, a three-phase contact shown in Figure 2-8 must form.

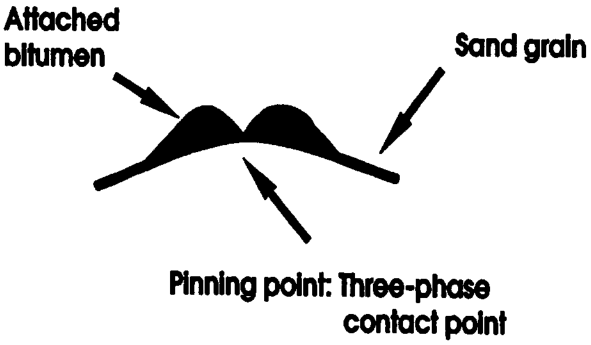

Figure2-8: Formation of the three-phase contact point (Masliyah, 2004)

(3) Bitumen recession along a sand grain surface

Following the formation of a three-phase contact, bitumen would recede along the sand grain surface as shown in Figure 2-9.

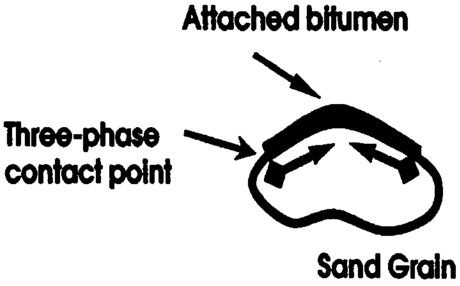

Figure2-9: Bitumen recession onto itself over a sand grain surface (Masliyah, 2004)

(4) Bitumen disengagement

Once the bitumen receded and formed a globule on the surface of the sand grain surface as shown in Figure 2-10, it needed to detach itself from the sand grain.

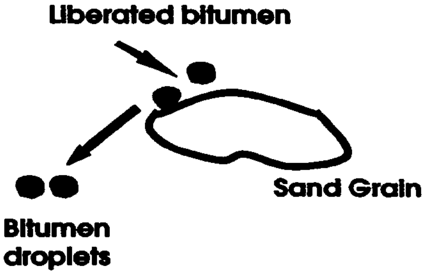

Figure2-10: Bitumen liberation from a sand grain (Masliyah, 2004)

There are many parameters that influence bitumen digestion. Eskin et al. (2000) built a theoretical model to study oil sand lump digestion. The process of digesting an oil sand lump moving in a heated water flow was considered. A lump was modelled as a heated sphere subjected to shear stresses and ambient temperature. Bitumen would melt when the combined effect of these two factors exceeded some critical value. This critical value was introduced in the form of a critical temperature, which could be determined from an experiment and was a constant in their model. They concluded from their study that the digestion rate significantly increased with an increase in water temperature and initial lump temperature. However, the most significant increase in the digestion rate was observed when the lump size decreased. Masliyah et al. (2004) pointed out that the slurry temperature affected the lump outer layer temperature, reducing the bitumen viscosity and also controlling the slurry viscosity. The lump size and its initial temperature also influenced the ablation process.

Another important parameter is the surfactants present in the slurry, which is controlled by the pH and the multi-valent metal ions in the aqueous phase. Surfactant can affect the interfacial tension of the bitumen-sand and bitumen-water, and water-sand contact angles, which in turn affects the formation of a three-phase contact angle, bitumen recession along a sand grain surface and disengagement. Drelich et al. (1994)

studied the surface and interfacial tension of the Whiterocks bitumen and its relationship to bitumen release from oil sands during hot water processing. The microscopic observations of the bitumen release from the Whiterocks oil sands for varying compositions of the aqueous phase showed that bitumen release from mineral particles strongly depended on the bitumen-water interfacial tension. Schramm et al. (2000) estimated that the optimum interfacial tension between bitumen and water was in the range between about 2 and 14mN/m. In 2003, they studied using an optimized system the interfacial tension between bitumen froth and corresponding clarified process water from bitumen extraction at 80 or 50°C. From their study for bitumen froth/aqueous tailings system, an interfacial tension of 6mN/m, 8 mN/m and 14 mN/m for the lean oil sand, for both the rich and mixed average/lean sands and for the average oil sand respectively.

In addition, the composition of the slurry and the degree of the mechanical shear play a role in bitumen liberation, because they affect the shear imparted on an oil sand lump. They also affect the formation of the three-phase contact point and certainly will affect the disengagement process.

2.2.3 Bitumen aeration

Bitumen aeration is a pre-requisite for successful bitumen flotation. The density of bitumen is so close to that of water, or maybe even greater, especially when some solids are attached to the bitumen droplet, that bitumen droplet cannot float without aeration to form bitumen froth. Air attaching to the bitumen droplet can reduce the density, helping bitumen to float to the top. Drelich et el (1995) studied the role of gas bubbles in bitumen release during oil sand digestion. Poor bitumen recovery from oil sand was observed when air was eliminated during digestion. Successful bitumen recovery was achieved when the oil sands were saturated with dispersed air during the digestion step. They suggested that the effective separation of bitumen from oil sands involved the mechanism of gas bubble attachment to bitumen located at the surface of mineral particle, spreading of bitumen over the gas bubble surface and detachment of bitumen-engulfed gas bubbles from the surfaces of coarse sand particles. Lowering the bitumen-water interfacial tension facilitated all these steps. This could be accomplished by an increase in pH and/or concentration of electrolytes.

The attachment of air to bitumen is controlled by the wettability of the bitumen and air bubbles surfaces. There are two ways that air bubbles could attach to the bitumen: (1) simple bitumen-air attachment. At low caustic levels or at temperatures below about 40-50°C, bitumen droplet attaches to air bubble at a discrete contact point, which does not spread to any great extent around the air bubble. (2) Air engulfing. When the temperature is sufficiently high, the bitumen flows over the surface of air bubbles to form a film around the air bubble. Adamson (1982) defined a spreading coefficient (S) to predict if a liquid could spread over a surface. A positive value of S suggests spontaneous spreading of the liquid over the surface, while a negative value implies "beading" of the liquid on the surface. For the bitumen spreading on the surface of an air bubble, an appropriate expression of the spreading coefficient is:

$$S = \gamma_{w/a} - \gamma_{b/a} - \gamma_{b/w}$$

where, $\gamma_{w/a}$ = interfacial tension between water and air bubble

$\gamma_{b/a}$ = interfacial tension between bitumen and air bubble

$\gamma_{b/w}$ = interfacial tension between bitumen and water.

It has been shown that bitumen has a positive spreading coefficient in water on air bubbles. But the spreading coefficient of bitumen could be zero, or even negative, due to the migration of surfactants, resulting in a decreased aqueous surface tension $\gamma_{N/a}$.

Leja and Bowman (1968) applied thermodynamic analysis to the Athabasca oil sands extraction system. In complex systems containing oil, water, solid, and gas phase, such as the Athabasca oil sands, a number of interfacial transformations occurred. The necessary interfacial transformations could be analyzed using a thermodynamic approach. From their thermodynamic analysis, they defined conditions that:

$\gamma_{o/w} + \gamma_{a/w} > \gamma_{a/o}$ for contact attachment

and $\gamma_{a/w} > \gamma_{o/w} + \gamma_{a/o}$ for filming

For the oil sands system, $\gamma_{a/w}$ was appreciably larger than the sum of the other interfacial tensions; Therefore both attachment and filming should invariably result.

Drelich et al. (1996) studied the bitumen spreading and formation of thin bitumen film at an air-water interface. Bitumen spreading over gas bubble surfaces was observed through a stereoscopic microscope for Whiterocks oil sand samples submerged in alkaline solutions. This phenomenon was also observed for the model systems where air bubbles were placed on the surface of a bitumen-coated quartz slide immersed in water. They concluded that after droplets of Whierocks bitumen containing10 wt. % kerosene attached to a gas bubble, a balance of interfacial tensions in the system favoured spreading of the bitumen over the entire gas bubble rather than formation of bitumen lenses. Bitumen spread over the air bubble surface because of a positive spreading coefficient. It seemed that the spreading coefficient reached a value close to zero when the system approached the equilibrium state. Microscopic observation showed that the initial spreading of a bitumen film precursor assisted the bitumen film spreading. This bitumen film precursor reduced the surface tension of the aqueous phase. Within the first few seconds of contact between the air bubble and bitumen, the bitumen film precursor covered the gas bubble surface at room temperature. The bitumen film slowly followed the bitumen film precursor. Although thermodynamic conditions favoured bitumen spreading over the gas bubble surface, discontinuities in the bitumen film appeared for certain conditions. The experiments by Drelich et al were performed with bitumen containing 10% kerosene, which would explain why the bitumen still spread over the air bubble at the low temperature, while other studies showed that below about 50°C, spreading of bitumen over the air bubble surface is extremely slow.

Alexander and Li (1996) studied the effect of bitumen films over air bubble surfaces on bitumen drop-air bubble attachment. The dynamic process of bitumen film formation on an air bubble surface, which occurred during the recovery of bitumen from oil sands, was studied by measuring the time and temperature dependence of bubble surface tension and contact angle. It was observed that the air bubble attached to bitumen immediately. After attachment, a thin bitumen film started to form around the surface of the air bubble. This film caused a decrease in the initial air-water interfacial tension, which eventually reached a plateau, as observed at room temperature, 50°C and 70°C. It was also observed that the formation of a bitumen film resulted in a change of contact angle between the air bubble and the bitumen surface, which eventually reached an equilibrium value. They concluded that as a result of the formation of a thin bitumen film on an air bubble surface, the apparent bubble surface tension initially decreased rapidly and gradually reached an equilibrium value. The time required for the complete formation of the film was shorter at higher temperatures.

There are also some hindrances to aeration. Moran et al. (2000) studied the factors affecting the aeration of small bitumen droplets. They believed that repulsive colloidal forces might prevent the formation of a three-phase contact line, which acted between bitumen and air across an intervening aqueous phase, hindering bitumen spreading on air bubbles. They also found that the probability of successful aeration was significantly reduced when solid particles (clays) were suspended in the aqueous phase. Other studies suggested that air bubbles at neutral or alkaline pH were negatively charged and therefore might resist contact with the negatively charged bitumen.

2.2.4 The role of natural surfactant

Even the earliest studies carried out by Clark and Pasternak suggested a need for surface-active agents to be present for good bitumen recovery. This need was fulfilled with the addition of alkaline additives. The surfactants are substances whose molecules consist of two well-defined sections: hydrophobic section (tails) is oil soluble, lacking affinity for water, while the hydrophilic section (heads) has a strong affinity for water. There are three main classes of surfactants: anionic surfactants with special reference to the partially unsaturated fatty acids, the cationic surfactants and non-ionic surfactants. Surfactants can affect the nature of a surface or interface in three major aspects that are significant to bitumen extraction. It can change the surface wettability, interfacial tension and the electric surface potential.

Moran et al. (2000) studied the variation of bitumen-water interfacial tension with pH. The aqueous phase was designed to simulate the chemistry of process water in a commercial oil sands extraction. Figure 2-11 summarizes the variation of interfacial tensions with pH. The interfacial tension exhibits a maximum at pH around 4, and deceases with increasing pH to 11.

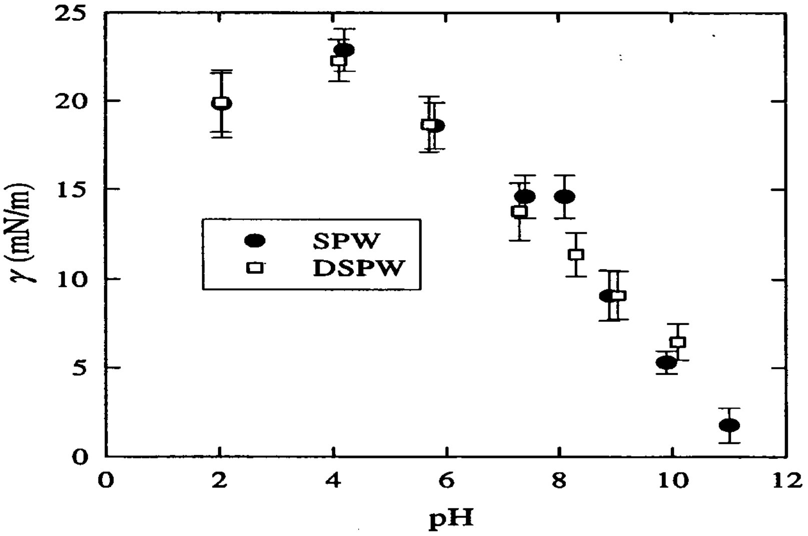

Figure2-11: Interfacial tension γ of bitumen-water systems as a function of pH.

SPW – simulated process water

DSPW –SPW with divalent ions (Masliyah et al 2004)

Basu et al. (1997) investigated the effect of pH on (a) bitumen film thinning and film rupture process, (b) bitumen/water contact line displacement, and (c) the static contact angle of bitumen on a glass surface in an aqueous medium. They found that the bitumen film thinned and ruptured spontaneously when a few drops of warm water (40°C) having a pH of 11 were added on top of the bitumen film. But with water having a pH of 3, the bitumen film did not thin or rupture. It was observed that the dynamic contact angle of the bitumen changed faster with time in the case of a lower pH and the static contact angle of the bitumen droplet increased with an increase in pH. They concluded that instead of operating the bitumen liberation process at a pH of 8.2, it would likely be better to make use of the fact the water pH affects the different steps of bitumen disengagement in different ways. A pH cycle could be designed for a faster film thinning and rupture, faster contact line displacement and large static contact angle.

The interaction of bitumen with sand, as a function of pH, particle size, temperature and solvent addition to bitumen, was studied by Dai and Chung (1995). It was observed that sand particles could be easily detached from the bitumen surface at pH > 6. At pH < 6, there was a strong attachment between bitumen and solids. It was also observed that the silica and bitumen were negatively charged at pH > 3. However, as the pH increased (pH > 5), the bitumen surface was more negatively charged than the silica. They concluded that increasing pH always favoured bitumen liberation.

Brown et al. (1980) examined the wetting behaviour of oil/water/silica systems, principally by measuring contact angles. Static contact angles were measured by the captive droplet technique and the capillary tube technique. The dynamic contact angles were obtained using the capillary tube method. They found that with an alkaline aqueous phase (pH 9), introduction of Forties crude oil into a glass capillary pre-filled with water resulted in a zero contact angle and this complete water-wetted state was maintained for many hours. With an acidic aqueous phase (pH 4), good wetting of the surface by oil was immediately apparent upon introduction of oil into an initially water-filled glass capillary. Over the neutral pH range, a more complex, intermediate range of behaviour was observed. It was concluded that the wettability of an oil/silica/water system is strongly pH dependent due to the activation of the surfactants by the aqueous phase.

Schramm et al.(2000) studied the influence of natural surfactant concentration on the hot-water process for recovering bitumen from the Athabasca oil sands. All the surfactant concentrations reported were determined using the complete foam fractionation/acid titration method. Their study showed that free surfactant concentrations, in particular total carboxylate salt concentrations increased linearly with increasing NaOH addition. In fact, only a small portion of the sodium hydroxide was consumed during an oil sand extraction, which actually generates sufficient amount of natural surfactants. Any limit to the concentration of free carboxylate surfactant, which can be generated by the addition of sodium hydroxide during the extraction of any type of oil sands, had not been observed. It was noted that a high-grade oil sand ore could supply a high concentration of free carboxylate surfactant in extraction without sodium hydroxide addition. A lean grade oil sand ore might not be able to supply sufficient amount of surfactant to produce any detectable concentration of surfactant in solution when moderate levels (up to 0.04%) of sodium hydroxide were added during the extraction. They found that there was a critical value of surfactant concentration, corresponding to the maximum in bitumen recovery. The bitumen recovery increased with free surfactant concentration until the concentration reached a critical value. After that, the bitumen recovery decreased with further increasing free surfactant concentration. They concluded that the surfactants generated in the hot water extraction process appeared to play a critical role in determining the maximum bitumen recovery.

2.2.5 The role of fine minerals

The content of mineral solids smaller than 44 μm is used as a measure of the "fines" content in an oil sands sample. Lean grade oil sand ore contains a large amount of fines and water. The water content of oil sands usually increases while bitumen content decreases with increasing fines content. Clay minerals are predominantly kaolinite, illite, and a small amount of montmorillonite, which only appears in the fines. Clark found that the recovery of bitumen deceased as the clay and silt content increased. Clark also believed that the small amount of clay was needed for the process to disperse the oil sufficiently enough so that it could attach to air bubbles and float. In the study carried out by Smith et al. (1992), it was found that increasing quantities of calcium clays increased the primary recoveries to a maximum before becoming detrimental. High fines ores have typically been a problem in the commercial plants. They give rise to high middlings densities, low recoveries and increased water content in the froth.

In a study by Moran et al. (2000), it was found that the steric stabilizers were largely fine clay particles that either adsorbed on the interfaces or were suspended in water between the bitumen drop and the air bubble. The presence of clays led to a significant decrease in bitumen aeration.

Kasonogo et al. (2000) investigated the effect of clay and calcium ions on bitumen extraction from Athabasca oil sands. The oil sands slurry was prepared in kaolinite, illite, or montmorillonite suspensions at 1 wt% level of clays on the basis of oil sands sample. The experimental results showed that introducing montmorillonite, kaolinite, or illite clays alone to a good processing ore did not impose any significant impact on bitumen recovery. Increasing calcium ion concentration up to 40 ppm, together with the addition of illite or kaolinite clays, did not interfere with bitumen flotation substantially. However the co-addition of 1 wt% montmorillonite clays and 40 ppm calcium caused a sharp reduction in bitumen recovery. It was concluded that the adverse impact of calcium ions and montmorillonite clays on bitumen recovery was associated with stronger affinity of calcium with montmorillonite clays than with kaolinite or illite clays. The calcium triggered clay deposition on bitumen and reduced the contact angle of water on bitumen.

Liu et al. (2004) studied the role of fine clays in bitumen extraction. Ion adsorption tests were conducted, where montmorillonite or kaolinite clay at 1g/L (clay/solution) was added to a 1mM calcium solution. Clearly, montmorillonite and kaolinite clays had different surface properties. Compared to kaolinite, montmorillonite clay exhibited a large capacity for ion adsorption from a solution. Similarly, there were some differences in the zeta potentials of kaolinite and montmorillonite clays. The zeta potential of a montmorillonite clay suspension did not show a noticeable change with pH form 3 to 11, while the zeta potential of kaolinite suspension decreased with increasing pH. In this study, they also measured colloidal forces between bitumen and fine clays and between bitumen and bitumen in the presence of montmorillonite clays. It was observed that the adhesion force between bitumen and montmorillonite was much stronger than the adhesion forces between bitumen and kaolinite, in particular, when calcium ions were present. The addition of montmorillonite clays and calcium diminished the adhesion forces between bitumen and bitumen. The zeta potential distribution study showed that in the presence of calcium ions, montmorillonite had a strong attachment to bitumen while kaolinite attached to the bitumen weakly. Strong attachment of montmorillonite to bitumen built a barrier for bitumen droplets to coalescence and to attach to air bubbles, resulting in a poor bitumen recovery.

2.3 The Current Knowledge on Oil Sand Weathering

2.3.1 Dehydration

Clark (1929) believed that the water in the ore, as an internal phase in the bitumen, was critical to the step of displacing the bitumen from the sand. He ascribed the oil sands weathering to the water loss from the oil sand matrix. He also believed that bitumen that contained water adhered less strongly to the mineral than it did for the dry bitumen. If the bitumen was dried and consequently processed poorly, it was treated with calcium oleate to improve the process. Research council workers had thought that the deterioration of oil sands was due to the loss of the natural water content or to the disappearance of the water film separating the oil from contact with the sand surface, thus allowing the oil to become directly attached to the sand. However, in another study carried out by Clark (1949), deterioration was connected with the clay content of the oil sands and with its association with bitumen. It appeared that the change in association between clay and bitumen took place without the loss of water from the oil sands.

Ali (1975) studied the ageing water phenomenon of oil sands. The result of his study indicated that the loss of connate water by evaporation was the major factor causing the poor processability of weathered ores. A possible explanation of the detrimental effects of losing indigenous water was the destruction of the structure of the oil sands formation. Removal of water resulted in a direct oil-solid contact and a deteriorated processibility.

Schramm and Smith (1987) concluded from their study that recovery loss due to the oil sand weathering was not due to dehydration of the oil sands.

Liu et al. (2004) examined oil sand weathering by artificially treating oil sands samples inside an oven at 50°C under controlled environment. Their results showed that more than 90% of weight loss during the treatment was due to the water loss of oil sands.

The consequence of the losing connate water was thinning or even the removal of the water film between the bitumen and the sand grains, leading to an increase in divalent ion concentration in the remaining connate water. The direct contact between bitumen and sand grains coupled with high concentrations of divalent ions in the connate water would undoubtedly make the sand grain surface more hydrophobic via the transfer of surfactants from bulk bitumen to the solids surface. They concluded that evaporation of the connate water during weathering/aging of oil sands, or loss of water from a water film at the solids surface, was one of the main reasons for the poor processability of weathered oil sands.

2.3.2 Oil sands oxidation

Wallace (1989) investigated the oxidation of sulfide minerals during storage of Athabasca oil sands. They suggested that the oxidation of sulphite during oil sands weathering led to acidic conditions that dissolved minerals and increased soluble divalent cations. These di-valent cations could increase bitumen-mineral attraction and coagulate fines, hence reducing flotation efficiency.

However a different study carried out by Schramm and Smith (1987) showed that there was no clear increase in sulphate or cation concentrations by oil sand weathering. Schramm and Smith explained weathering of oil sands in terms of changes in surfactants. From their experiments, an effective reduction in the carboxylate-producing tendency by weathering was observed. Weathering caused an increase in the amount of NaOH addition needed to attain the critical concentration of free cayboxylate surfactant. Some reactions occurred during oil sands weathering. These reactions either affected the source of surfactants or produced a species which would react to consume NaOH in the extraction process. In their later study, they concluded that the reduction of the surfactant concentration was not due to the loss of light ends from bitumen, dehydration of oil sands, and oxidation of organics or decomposition of the surfactant themselves. The polyvalent metal species released from mineral oxidation during oil sand weathering either reacted with NaOH, preventing it from reacting to produce free carboxylate surfactants, or reacted with surfactants directly, complexing the surfactants.

Munoz et al. (2003) discussed the microscopic morphologies of bitumen from various sources and their relationship to ore processability. The extensive microscopic work had demonstrated that the bitumen in an oil sand ore was the phase most susceptible to oxidation and that the resulting changes manifested themselves in particular microscopic structure. Oxidation might have been the main mechanism responsible for the naturally occurring bitumen degradation in bitumen froth. The changes of bitumen could have significant impacts on processibility, well before any concomitant changes were observed in the mineral chemistry.

Chapter 3: Experimental System and Procedures

3.1 Experimental Systems

The foundation of this work is to build up a laboratory oil sands treatment system. Inside this system, oil sand should be artificially weathered under the controlled conditions. Figure 3-1 shows the oil sands treatment system for this research work.

An air or a nitrogen gas stream from a gas cylinder goes through a gas flow meter so that the flowrate of input gas can be controlled. In most cases, the input gas into the oven is water –saturated, especially when the oil sands samples are treated inside the oven to ensure a negligible water loss from the samples. With water-saturated gas at controlled saturation level by adjusting the input temperature of the gas, the water content remained in the treated oil sands could be controlled. A large flowrate of input gas could cause the gas to be un-saturated because the resident time of gas in water is insufficient for mass transfer between the water and gas. A flowrate that is too small could result in ineffective treatment of the oil sands samples.

Two saturation bottles filled with de-ionized water are used for water saturation of the gas. One bottle is held at room temperature while the second one is placed inside a thermal bath. To increase the efficiency of water saturation, spargers are used to generate smaller bubbles for better mass transfer. The temperature of input gas is controlled by adjusting the temperature setpoint of the thermal bath.

To investigate the role of ore oxidation on oil sands processability, nitrogen treatment is also performed in this research. In this case, the oven has to be vacuumed first to remove air inside the oven. After the air has been removed, the oven is flushed with pure nitrogen. A vacuum oven has been chosen in this experimental system. The temperature of the oven is always set to 60°C, since it was found experimentally that at this temperature, the oil sands samples could be effectively weathered inside the oven in one week.

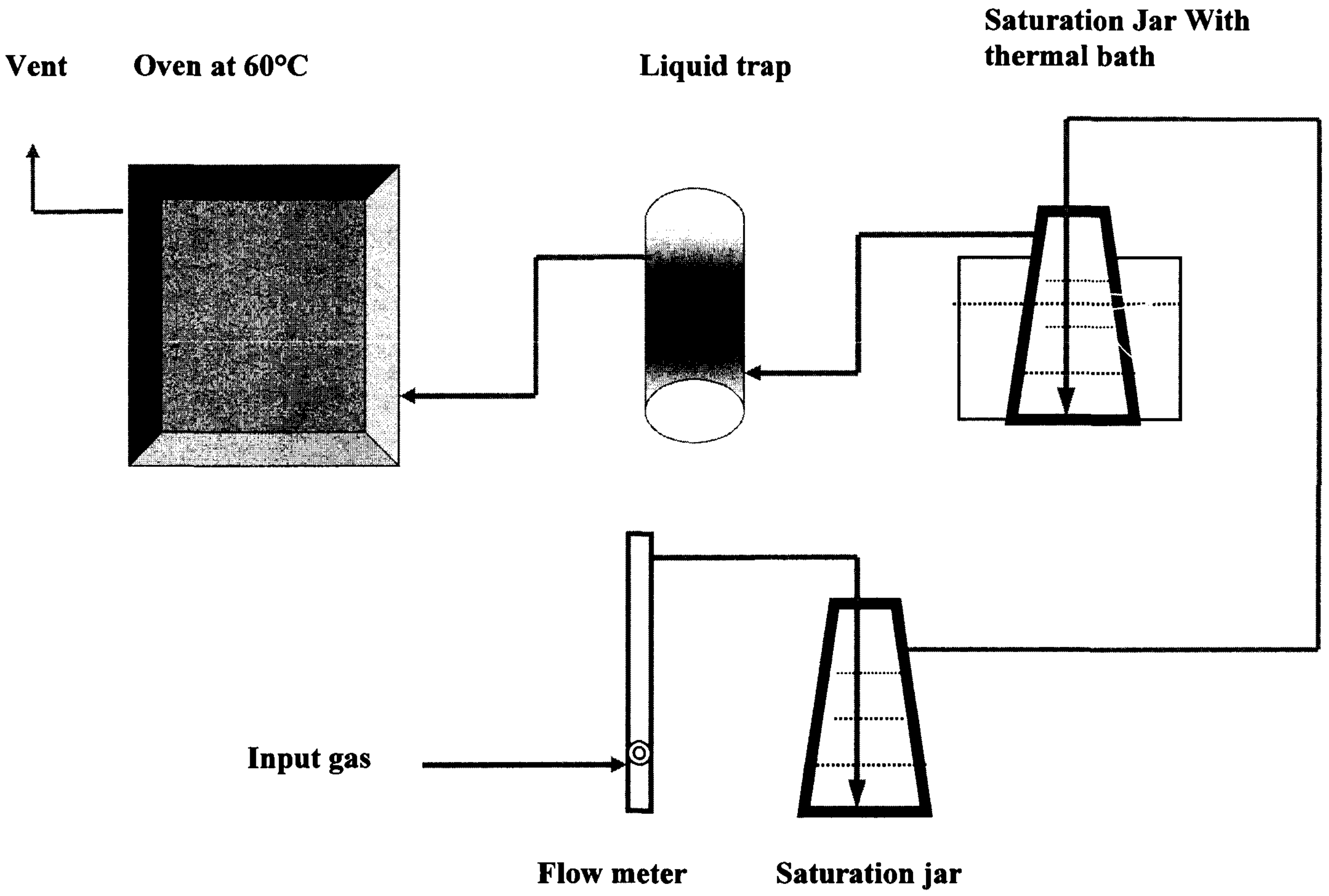

Figure 3-1: Schematics of experimental system

3.2 Experimental Procedures

3.2.1 The procedure of air treatment

Weathering of the good processing ore was carried out in a well-controlled oven under different conditions. The oven temperature was set at 60°C and the input air temperature changes depending on the requirement of the experiment. For the dry-out experiment, the input air temperature was about 20°C. The oil sands samples inside the oven were dehydrated because the air inside the oven was not water saturated.

To avoid water loss by the treatment, the input air temperature was set around 68°C (ignore the heat loss between the thermal bath and oven). The solubility of the water in the input air at 68°C was higher than that in the air inside the oven at 60°C. In this case, there was no water-loss for oil sands samples during the treatment. To make sure this treatment was successful, a beaker containing a sufficient amount of water was placed inside the oven. To ensure the water content remained in the treated ores, the input air temperature was controlled between 60°C and 68°C. When the oven temperature reached 60°C and the bath temperature reached the desired temperature, the system was kept running for about 1 hour to ensure the experimental system at a steady state. Oil sands samples of 350g each were placed in an alumina tray as a layer of about 0.5cm thick. After the experimental system reached steady state, the oil sands samples were inserted into the oven for a week.

3.2.2 The procedure of nitrogen treatment

The procedure of nitrogen treatment is quite similar to that of air treatment. However, nitrogen treatment requires air removal from the oven and maintenance of an inert atmosphere inside the oven throughout the treatment. Therefore, oven vacuum and nitrogen flush are vital for this procedure. For the dry-out and partial water-loss experiments, 350g of oil sands placed in an alumina tray as a layer of 0.5cm thick was inserted into the oven at room temperature. The oven was first evacuated quickly so that over a short period, the pressure inside the oven dropped to -6 inch Hg. Then, the nitrogen was allowed into the oven at such a large flowrate that in several minutes the pressure inside the oven reached atmospheric pressure. The oven was flushed with nitrogen for 4 hours at room temperature. The thermal bath was started to ensure the input nitrogen was water-saturated at desired temperatures. After the bath temperature reached a desired value, the oven was heated up to the temperature set-point of 60°C and kept at this temperature for one week.

For the experiment without water loss, 350g of oil sands was placed into a flask. The flask was flushed with nitrogen and covered with a stopper. The oil sands samples inside the flask were then placed into the oven at room temperature. The flask was tightly tied onto the oven shelf. The oven was rapidly evacuated until the pressure inside the oven drops to 6- in Hg. Then the oven was filled with nitrogen to an atmospheric pressure. The oven at room temperature was flushed with nitrogen for 4 hours. The pressure inside the oven was kept slightly higher than the atmospheric pressure. The nitrogen was connected to the saturation bottle. The stopper is removed from the flask to start the weathering. The treatment lasts for one week.

3.2.3 Flotation procedure

In this study, a Denver cell was used to separate bitumen and solids. The froth and tailings were collected for further analysis. A typical Denver cell is shown below:

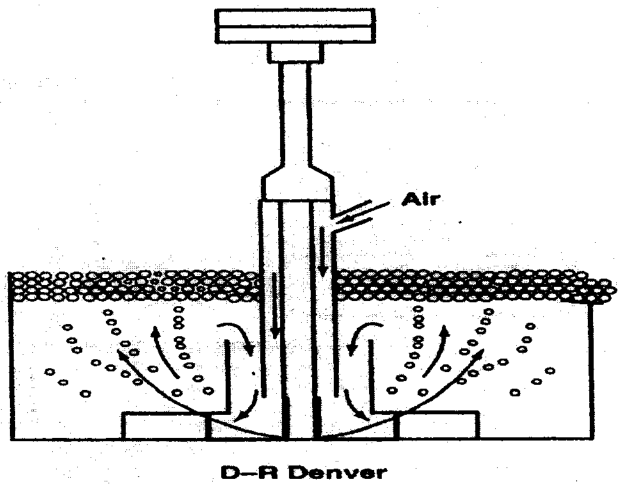

Figure3-2: Denver Cell

Air is injected through a central shaft into a stator. When it goes through the high shear region between the rotor and stator, the air is dispersed into fine bubbles. Bitumen is liberated from the solids under the shear force at certain temperatures. The collision between the liberated bitumen droplets and the air bubbles takes place. The bitumen droplets attach to air bubbles and float to the top the vessel, forming bitumen froth.

The procedure of Denver cell flotation is very important for bitumen recovery tests. In this study, when the power of the Denver cell was on, 1000ml of de-ionized water or processing water from the industry at 35°C was poured into the cell. This temperature was maintained throughout the experiment by a thermal bath. 200g of the treated samples were placed into the cell. The agitation was started and continued for 5 minutes. During this oil sand conditioning stage, no froth was collected. The air was injected into the cell while the slurry was under agitation and the froth was collected for 16 minutes. Below is a summary of flotation conditions:

- 1-liter Denver flotation cell
- 200g of F11B ore sample (bitumen: 14.5%; H_2O: 4.0%; Solids: 81.5%)

- Conditioned in 1000ml DI water at 1500rpm and 35 °C for 5min
- Flotation with 25ml/min air injection
- Temperature held constant at 35 °C for the entire experiment

3.2.4 Procedure for the hydrophobicity study of solids

(i) Clean Solids Extraction

To analyze the hydrophobicity of solids, clean solids must be extracted from oil sands samples. 30g of sample (treated or original) was placed into a glass tube. The tube was then filled with toluene and shaken for 30 minutes by a shaker. The solids in the tube were allowed to settle for about 5 minutes. Then the toluene in the tube was removed carefully, replaced by clean toluene. The tube was shaken again for another 30 minutes. This process was repeated until the toluene inside the tube was colorless. The clean solids were kept in toluene to prevent possible oxidation.

(ii) Procedure to take pictures of solids

Pictures were taken to visualize the hydrophobicity of solids. About 2g of clean solids were placed into a small glass bottle. 10 ml of de-ionized water was added into the bottle so that more than half of the bottle was full. The toluene was carefully removed from water surface. About 10ml of heavy mineral oil was added into the bottle until whole bottle was full. There are three phases inside the glass bottle at this stage: the solid phase on the bottom of the bottle, the water phase in the middle and the oil phase on the top. The bottle was sealed and shaken for 1 minute. The hydrophilic solids will stay in water phase while the hydrophobic solids will go to the oil phase. For the dry-out experiment, almost all the solids went to the oil phase right after shaking the bottle. In this case, the pictures were taken right away. For other experiments, the contents of the bottle were allowed to settle for two days prior to taking pictures.

(iii) Procedure to measure the percentage of solids in water phase

To quantify the change in hydrophobicity of the oil sands solids after treatment under different conditions, the solids distribution between the water phase and oil phase was determined by measuring the percentage of solids in water phase. About 3.5g clean solids were placed into a small glass bottle. 10 ml of de-ionized water and 10ml of heavy mineral oil were added to the bottle. The bottle was shaken for 1 minute so that hydrophilic solids stayed in the water phase and the hydrophobic solids went into the oil phase. The contents were allowed to settle for 1 hour to ensure complete phase separation. The oil phase on the upper part of the bottle was carefully removed. The bottle was filled with de-ionized water so that water phase occupied slightly more than half of the bottle then 10 ml of heavy mineral oil was added. The bottle was shaken for 1 minute and allowed to settle for 1 hour. The oil phase was removed. This process was repeated until no solids went to the oil phase. Slowly, the whole bottle was filled with de-ionized water to replace the oil phase by overflow. The solids inside the water phase were dried and weighted.

3.2.5 Procedure for the reversibility study of the weathering process

The reversibility of oil sands weathering is studied in this work. 350g of original oil sands sample were placed in a pan as a layer of about 0.5 cm thick. The pan was inserted into the oven at 60°C and the input air temperature was at 20°C. The samples were treated for a week. After treatment inside the oven, each 200g treated sample was placed into a glass jar. 500ml of de-ionized water is placed into each jar, totally covering the oil sand sample. After a certain designated time, the oil sands sample was placed into a Denver Cell and 500ml of de-ionized water was added. The Denver Cell was heated to 35°C and a flotation test was performed.

Chapter 4: The Characterization of Experimental Samples

4.1 Materials Handling

The oil sands samples used in this work were F11B, from the North Mine at Syncrude. The samples were placed in plastic bags and shipped to our lab. Each bag contained about 600g of oil sands. Once received, the oil sands samples were put into a freezer at -29 °C. The test samples were randomly chosen and defrosted under ambient environment for two hours before each treatment or test.

The process water was from Syncrude and arrived sealed in plastic pails when arrived.

4.2 Bitumen, Solid and Water Content of F11B

The soxhlet extractor- Dean Stark procedure is commonly used to determine the bitumen, water and solids contents. This procedure can dramatically increase the extraction rate as the sample is in contact with fresh hot solvent. A 100g of oil sands sample is weighed and placed in a paper thimble, which is in turn placed into the extractor. The extractor is connected to a round bottom flask containing the extraction solvent. A condenser is connected above the extractor. When the flask is heated on the bottom, the solvent is boiled up. The vapors of the solvent and water in the oil sands sample will rise and pass through the bypass arm of the extractor to the condenser, where they are condensed into liquids and fall into the side arm of the extractor. The water phase gathers on the bottom of the side arm and the solvent is on the top. Once the condensed liquid reaches the top of the side arm, the reflux of toluene goes back into the lower flask and extracts the bitumen into the toluene reservoir. The solvent is re-boiled, and the cycle repeats until the reflux of solvent through the thimble is colorless. At this point, the sample is completely extracted.

The water trapped inside the side arm of the extractor is separated from the condensed solvent and weighed. The bitumen and solvent collected is place into a 250ml volumetric flask and the volume is adjusted to 250ml by the addition of fresh toluene. The bitumen solution is placed into centrifuge tubes and it is centrifuged at 4000rpm to remove the solids. Exactly 5ml bitumen solution is taken from the centrifuge tube by pipette and spread on a weighed filter paper. The filter paper then is hung up to allow for complete evaporation of the solvent for one day. The dried paper is weighed again to allow the determination of bitumen content. The solids partition into two parts: most solids remain within the thimble while some fine solids settle when the diluted bitumen is centrifuged. The latter will be washed with fresh toluene until they are clean. Then the solids are placed into an oven at 110°C to remove the residual solvent. After cooling, the solids are weighed. Mass balance is used to check the final results.

Through the testing, the composition of F11B is: Bitumen content is 14.5%; water content is 4.0% and solids is 81.5%. The detailed testing results are shown in Table 4-1 and the contents of bitumen, water and solids for F11B are shown in Table 4-2.

Table 4-1: the results of the composition testing of F11B

Test No.	Sample wt. (g)	Bitumen (g)	Water (g)	Solids (g)
1	101.9	14.5	4.3	81.5
2	101.0	14.8	3.9	81.4
3	100.9	14.8	3.9	81.4

Table 4-2: The contents of bitumen, water and solids of F11B

Test No.	Bitumen (wt. / wt. %)	Water (wt. / wt. %)	Solids (wt. / wt. %)
1	14.3	4.3	81.4
2	14.7	3.9	81.4
3	14.5	3.9	81.6
Average	14.5	4.0	81.5

4.3 Size Distribution of Solids

(1) Solids Extraction

The Dean Stark procedure is used to extract the solids from the oil sands samples. The same solids extraction process as in content analysis of oil sands is used. Since some solids may still associate with bitumen after the Dean Stark extraction, further cleaning of the solids is necessary. For this purpose, 100g of solids are placed into a glass jar. The jar is then filled with fresh toluene and placed on a mixer. After shaking for an hour, the toluene solution is removed from the jar and centrifuged at a rate of about 4000rpm. The solids collected from the centrifuge tube are placed back to the jar. This process is repeated until the toluene solution is clear. The jar with solids is kept in a vacuum oven at 110°C for overnight to allow toluene to evaporate completely.

(2) The Mastersizer

A Mastersizer 2000 is used to measure the particle size distribution of solids samples. In this instrument, an optical device captures the actual scattering patterns from a field of particles. Using the Mie theory the size of particles that created that pattern can be calculated.

(3) Testing Procedure

The preparation of the sample before it is added to the system can be critical. If the sample is not well dispersed, dissolving, floating on the surface and is not representative, the results will not be correct. First, using a spoon, gently stir the solids inside the jar and break any aggregates of the solids. Then, hold the jar in both hands and gently roll the jar, continually changing its orientation for an about 20 seconds. At this time, 20 grams of the samples are taken out of the jar and placed into a beaker with 100 ml de-ionized water for 24 hours. Sodium silicate (0.1 w/w solution) is placed into the beaker. The suspension in the beaker is stirred with a mixer for a better dispersion. After the sample is well dispersed, the particle size distribution of the sample is determined.

(4) The Result

The results are shown in Table 4-3. Through the tests, the average fines content of the samples used in this study is about 10%.

Table 4-3: The test results of solids size composition of F11B

Test No.	- 44 μm (vol. %)	– 100 μm (vol. %)	– 200 μm (vol. %)	– 316 μm (vol. %)	-632 μm (vol. %)
1	9.49	10.53	38.34	78.97	100.00
2	9.96	11.12	39.24	79.60	100.00
3	10.23	11.48	39.35	79.47	100.00
4	10.47	11.80	39.83	79.76	100.00
5	10.54	11.85	40.16	80.11	100.00
Average	10.14	11.36	39.38	79.58	100.00

4.4 Weathering of Samples

Different type of oil sands may have different processability when weathered. Usually the recovery from a good processing ore will decrease and its froth quality will deteriorate when weathered. This phenomenon was observed even on the earliest work carried out by Clark. However, the recovery for some low-grade oil sands might be improved when it is weathered. It is therefore important to choose a suitable sample for studying ore weathering. Ideally we should choose an ore of weathering character no matter whether it is weathered at room temperature or in an oven at 60°C.

(i) Weathering Character of F11B at Room Temperature

In this study, 350g of F11B oilsands samples was placed inside a pan as a layer about 0.5cm think and then placed into the oven. The temperature of the oven was 25°C and the input air was at room temperature. After the treatment of 7, 30, 70, 90 days, the processability of the weathered samples was tested. Both recovery and froth quality were examined. The test results are shown in Table 4-4 and 4-5. Usually, two parallel tests were conducted unless the errors are big. In this case, the third or more tests were required.

The recovery from the original F11B is 92.6%. After 7 days of treatment, the recovery drops to 81.6%. It is clear from Figure 4-1 that the recovery decreases with increasing weathering time. Figure 4-2 shows that the bitumen/solids ratio also decreases with increasing weathering time. Clearly, the froth quality of F11B deteriorates when it is weathered. We can conclude that F11B is appropriate for this study.

Table 4-4: The test results of F11B weathered at 25 °C

Treatment time (days)	Sample weight (g)	Bitumen in froth (g)	Solids in froth (g)
0	297.0	39.6	2.2
	300.0	40.9	2.5
Average	298.5	40.3	2.4
7	200.7	23.4	1.8
	200.7	24.1	1.6
Average	200.7	23.8	1.7
30	200.1	16.9	2.8
	200.2	17.9	2.9
Average	200.2	17.4	2..9
60	200.9	8.1	2.0
	200.7	9.6	2.2
Average	200.8	8.9	2.1
70	300.8	11.0	2.9
	300.7	13.1	4.4
Average	300.8	12.1	3.7

Table 4-5: The recovery and forth quality of F11B weathered at 25°C

Treatment time (days)	No. of test	Recovery (%)	Bitumen/Solids ratio
0	1	91.9	17.9
	2	93.8	16.5
	Average	92.8	17.2
7	1	80.5	12.7
	2	82.7	15.2
	Average	81.6	14.0
30	1	58.4	6.1
	2	61.6	6.3
	Average	60.0	6.2
60	1	27.9	4.0
	2	32.9	4.4
	Average	30.4	4.2
70	1	25.2	2.9
	2	30.0	4.4
	Average	27.6	3.6

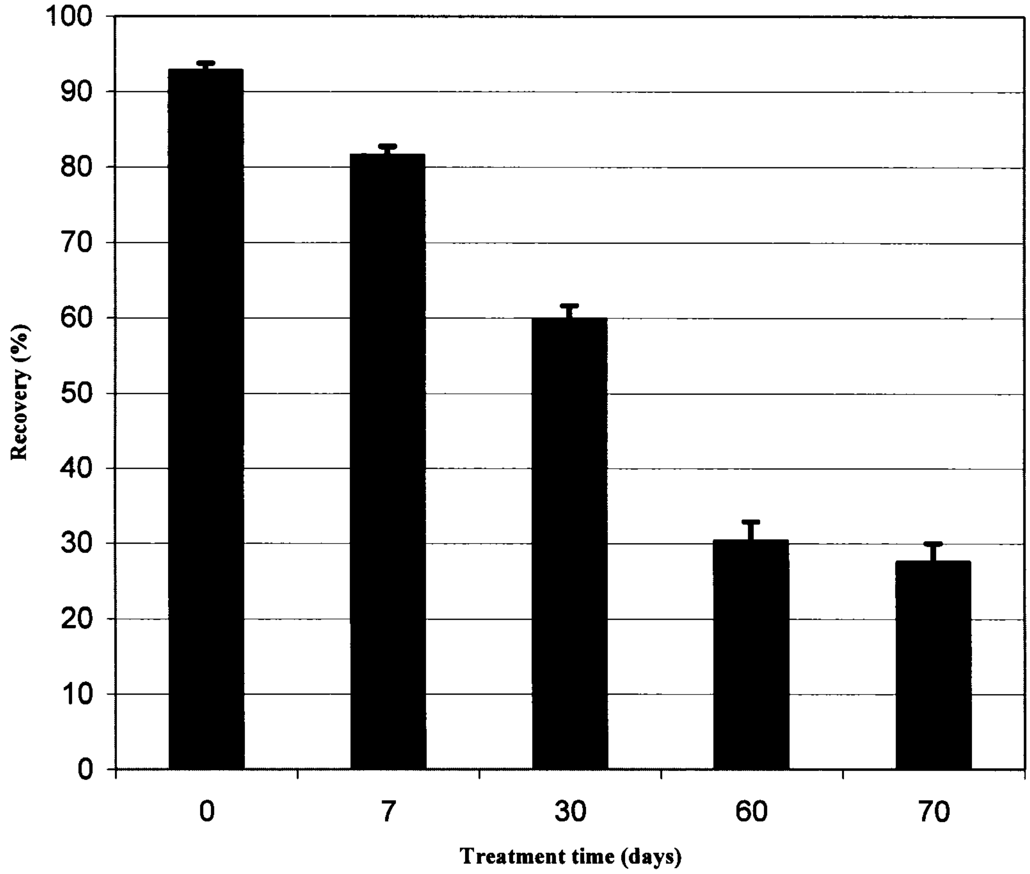

Figure 4-1: Recovery of F11B as a function of treatment time at 25°C

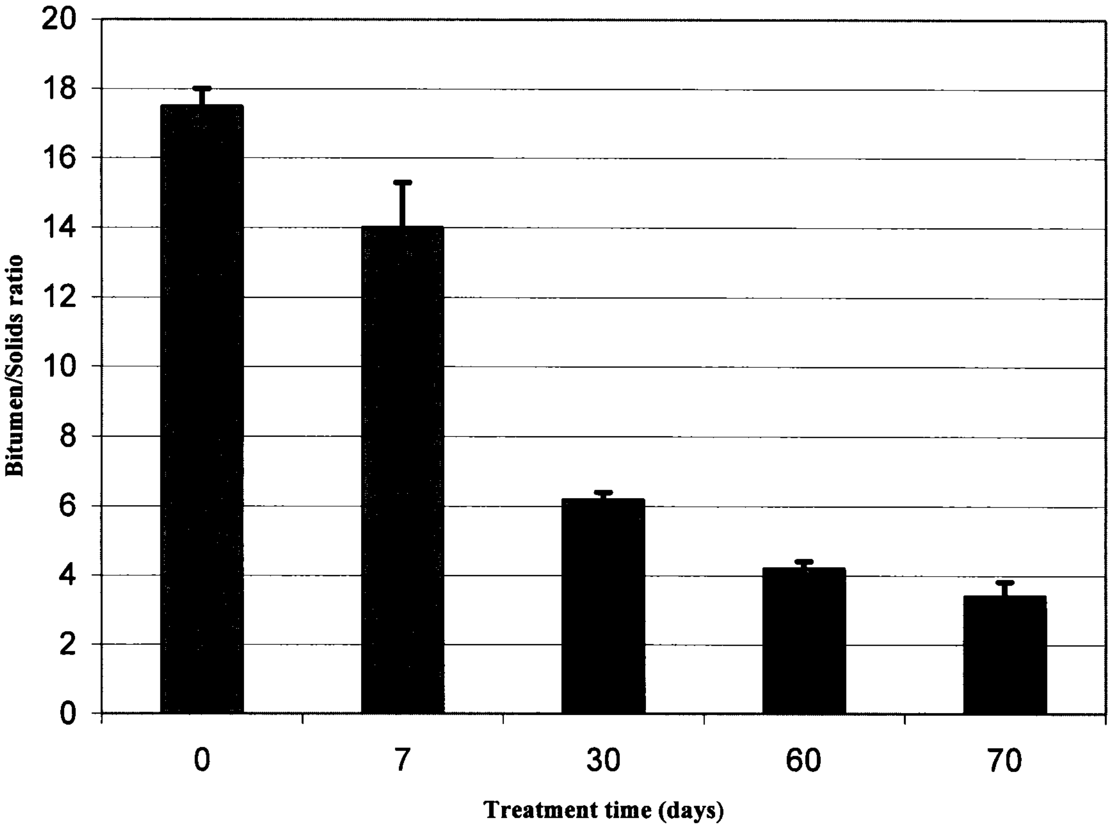

Figure 4-2: Bitumen/solids ratio as a function of treatment time at 25°C

(ii) High Temperature Weathering

Obviously, it is important to speed up the oil sands weathering process for the purpose of a lab study. A treatment temperature of 60°C might be highest temperature to treat oil sands sample in an oven without significantly altering the sample. At 60°C, F11B is treated for 1 day, 3 days and 7 days, respectively. The results in Tables 4-8 and 4-9 show after 7 days treatment in the oven at of 60°C, the bitumen recovery drops from 92 % to 6% and the froth quality deteriorates with increasing treatment time. F11B is well weathered under this treatment condition. For this study, the treatment conditions will be set to:

(a) Treatment temperature, 60°C

(b) Treatment time, 7 days.

Table 4-6: The test results of F11B weathered at 60°C

Treatment time (days)	Sample weight (g)	Bitumen (g)	Solids (g)
1	302.8	34.2	19.2
	302.0	31.2	20.3
4	300.8	7.7	5.9
	300.8	9.2	6.8
7	200.3	2.0	19.5
	200.2	1.6	16.1

Table 4-7: The recovery and forth quality of F11B weathered at 60°C

Treatment time (days)	No. of test	Recovery (%)	Bitumen/Solids ratio
1	1	77.9	1.78
	2	71.2	1.53
	Average	74.5	1.66
4	1	17.5	1.29
	2	21.0	1.34
	Average	19.3	1.32
7	1	6.8	0.10
	2	5.5	0.10
	Average	6.2	0.10

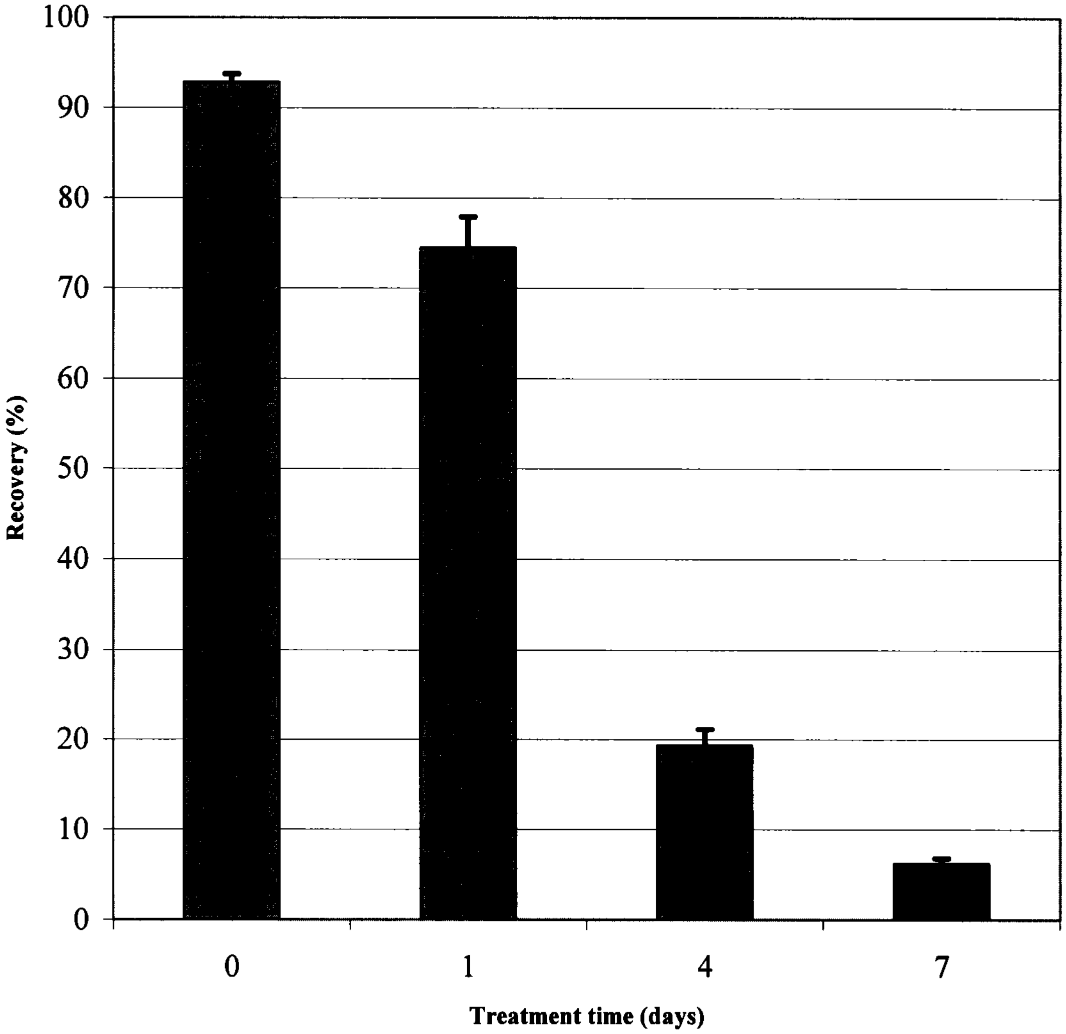

Figure 4-3: Recovery of F11B as a function of treatment time at 60°C

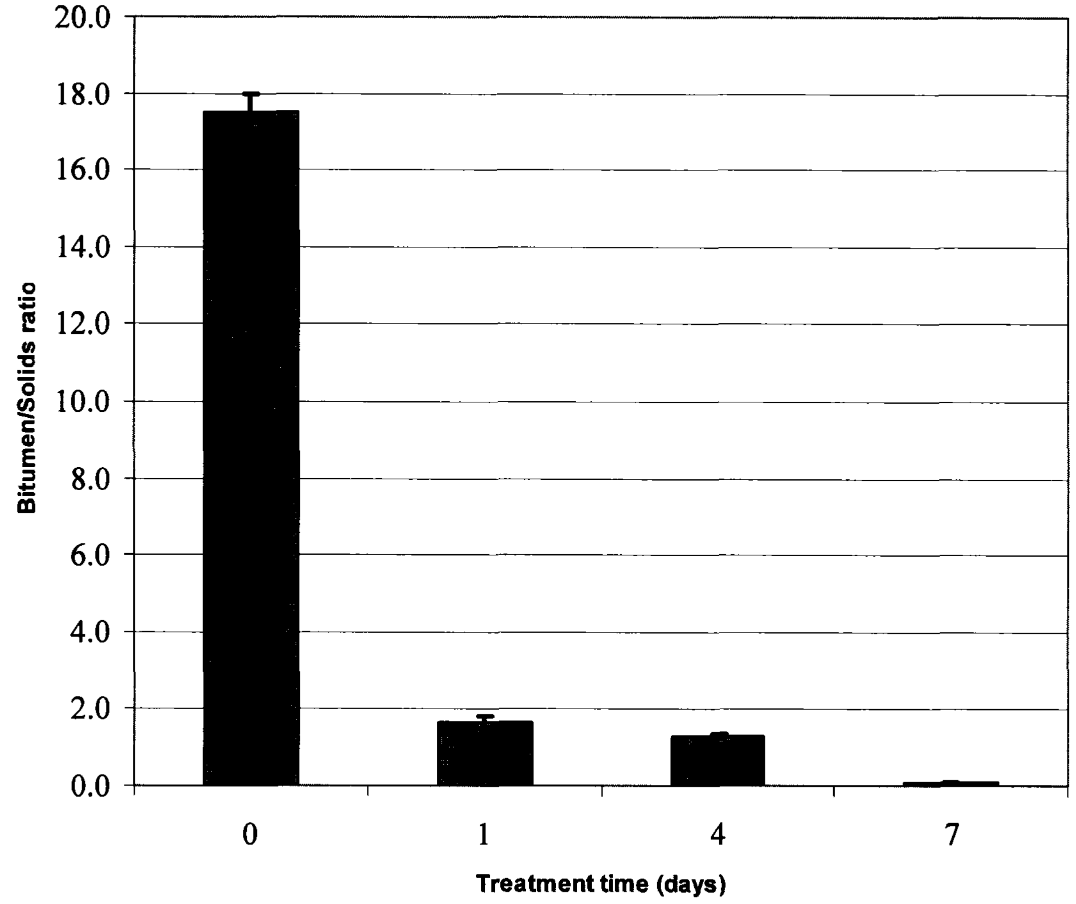

Figure 4-4: Bitumen/solids ratio as a function of treatment time at 60°C

Chapter 5: Results and Discussion

5.1 Effect of Water-Loss on Oil Sands Weathering

During the early days of oil sands development, research workers came up with an idea that the water-loss in oil sands during weathering caused bitumen recovery to decrease. However, Clark (1949) performed an experiment where he sealed the oil sands in a glass jar for several months and then tested its processability. He believed that water-loss was not the reason for the oil sands weathering. In 2004, Liu suggested that water-loss could be one of the reasons for oil sands weathering. He treated oil sands samples inside an oven at 50°C and injected air at room temperature into the oven so that all the connate water of the oil sands sample would be evaporated during the artificial weathering process.

The purpose of the experiments designed for this study is to investigate the relationship between the processability and remaining water content of treated samples.

Table 5-1 shows that the recovery of treated samples change with different remaining water contents. For the dry-out experiment, all the connate water inside the treated ores was evaporated and the treated ores were almost un-processable. The recoveries of treated ores were only about 6%. Very little froth formed during the flotation test. For the experiment without any water loss, all the connate water of treated ores remains. In this case, the recoveries of treated ores decreased from original 92% to 63.5%, but much higher than the case of complete water loss. During the flotation test, a thick bitumen froth layer formed on the top of slurry. For the experiments between these two extreme situations, the connate water of treated ores partially remained. The recoveries of treated ores decreased with decreasing remaining water contents in the samples, as shown in Figure 5-1.

It is generally believed that there is a thin water film between bitumen and sand grains in oil sands structures. This thin layer of water is critical for the hot-water process to work. Without the water film, it may be impractical to process oil sand. This may explain why Utah oil sand cannot be processed commercially. It was observed in our dry-out experiments that bitumen did not liberate from the sand grains. The appearance of the solids in the tailing water looked much like the fresh untreated oil sands samples. In this case, the sample was treated inside a 60°C oven with air injected at a temperature of 20°C. Under this treatment condition, the connate water in the oil sands is totally evaporated and the water film is thus completely destroyed. The bitumen directly attaches to the sand grains.

With the artificial weathering without water loss, the bitumen was liberated from the sand grains during flotation tests. However some bitumen did not float to the top of the cell and instead formed a layer of bitumen on the tailing solids. This finding suggests that water-loss is not the only factor responsible for poor processability of weathered oil sands. There might be other reasons such as oxidation of the oil sands that needs to be considered.

The results from the weathering experiment with partial-water-loss experiments imply that the partial water film might be destroyed as a result of bitumen connate water evaporation.

Table 5-1: Bitumen recovery of weathered ores with air treatment

Test No.	Sample wt. (g)	H_2O content (g /100g sample)	Bitumen in froth (g)	Recovery (%)
Dry-out				
1	200.3	0	1.99	6.8
2	200.2	0	1.60	5.5
Average	200.3	0	1.78	6.2
Partial water-loss				
1	292.6	0.31	5.57	15.7
2	293.5	0.62	10.56	22.3
Average	293.1	0.47	8.07	19.0
Partial water-loss				
1	200.3	1.87	9.43	32.2
2	200.3	1.68	7.47	25.6
Average	200.3	1.78	8.45	28.9
No water-loss				
1	201.1	4.01	19.17	65.8
2	205.9	4.01	18.28	61.2
Average	203.5	4.01	18.73	63.5

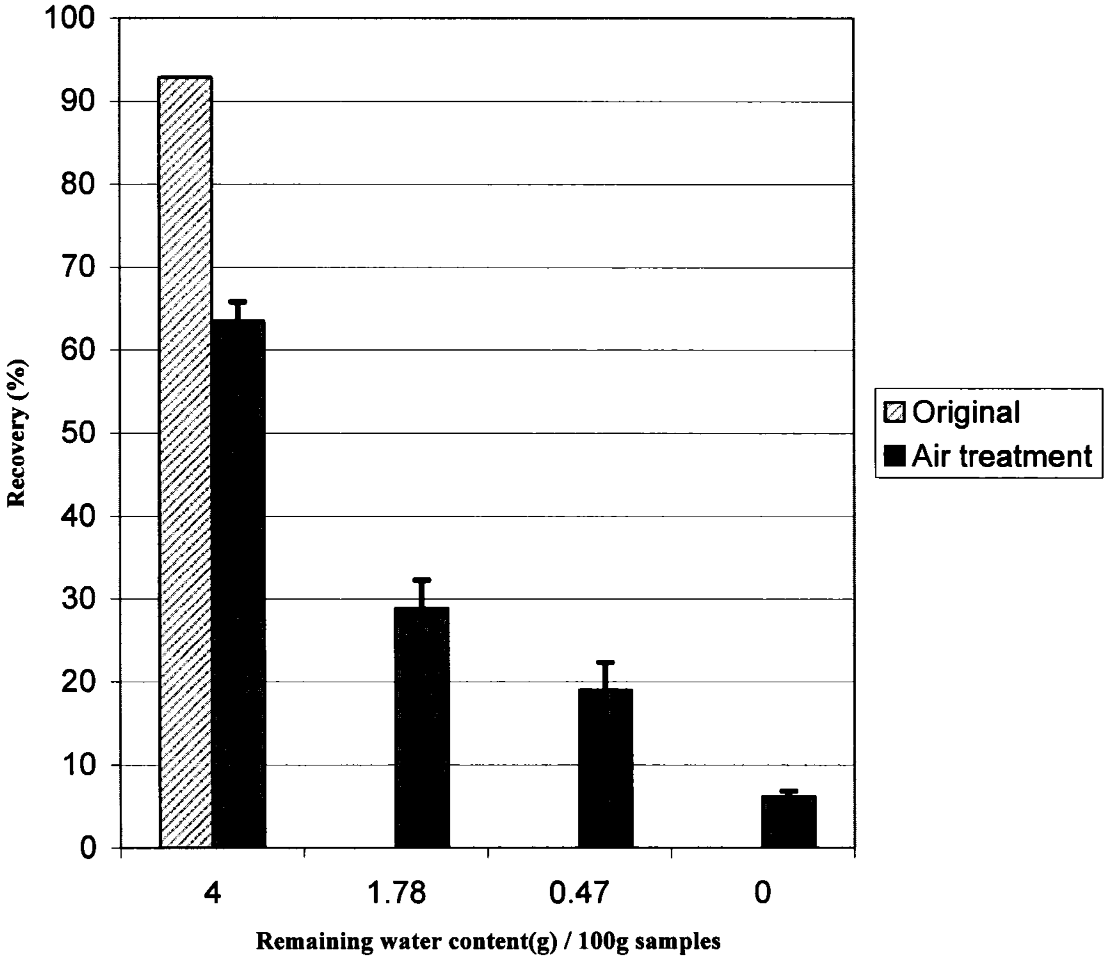

Figure 5-1: Recovery as a function of the remaining water content in weather ores by air treatment

5.2 Effect of Oxidation on Oil Sand Weathering

Water-loss is definitely a factor responsible for oil sands weathering. Apart from that, oxidation may also play a role. To confirm this, nitrogen treatment was designed and carried out. The test results are shown in Table 5-2.

The processability of treated oil sands ores varies with the remaining water content even though nitrogen (instead of air) was used to treat the samples. For the dry-out experiment, where the connate water in the treated ores was almost completely evaporated, the treated ores exhibited extremely poor processablities. The recovery of the treated ore was as low as 7.7%. The appearance of solids in the tailings water looked dark, similar to fresh untreated oil sands sample. No bitumen forth layer formed at the top of the flotation cell during the flotation test. With increasing remaining water content in the treated ores, the processability was improved. For the weathering without water loss, the highest recovery (up to 86.8%) is obtained. In this case a thick forth layer formed on the surface of the slurry.

Figure 5-2 shows that the recovery decreases with decreasing remaining water contents. This is the same trend between recovery and remaining water content obtained in air treatment experiments. The role of water-loss in oil sand weathering is confirmed, again, by weathering in nitrogen environment.

To elucidate the effects of oxidation on oil sands weathering, the test results under air treatment are compared with those under nitrogen treatment. There is no obvious recovery difference between air treatment and nitrogen treatment for the dry-out experiments. Under the treatment condition for dry-out experiment, the connate water inside the oil sands sample is almost completely evaporated. The water film between the

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To elucidate the effects of oxidation on oil sands weathering, the test results under air treatment are compared with those under nitrogen treatment. There is no obvious recovery difference between air treatment and nitrogen treatment for the dry-out experiments. Under the treatment condition for dry-out experiment, the connate water inside the oil sands sample is almost completely evaporated. The water film between the bitumen and sands grains, which is vital for bitumen extraction with hot water technology, is destroyed so that the bitumen directly attaches to the surface of sand grains. If the water film is destroyed, no matter whether the oil sands was treated with air or nitrogen, the processability of treated ores will be very poor since bitumen will not be liberated from the sand grains during bitumen extraction compared to the water film loss. Other factors seem less significant.

However, the recovery obtained from the samples with nitrogen treatment is much higher than that from samples subjected to air treatment without any water loss. Since only negligible water loss was involved, it would be safe to assume no connate water loss during the treatment and the water film was kept intact. As observed experimentally for both cases, bitumen was well liberated from the sands grain during flotation. The only factor, which makes such a big recovery difference, was that different gases were used to treat the oil sands samples. Air clearly showed much higher impact on the oil sands weathering than nitrogen.

Figure 5-2 shows that although the recovery curves of nitrogen treatment and air treatment share the same trend (the recovery decreases with decreasing remaining water content), the curve of nitrogen treatment is above that of the air treatment. It could be concluded that oxidation of oil sands plays a significant role in oil sand weathering.

Table 5-2: The experiment results of recoveries by Nitrogen treatment

Test No.	Sample wt. (g)	H_2O content (g /100g sample)	Bitumen in froth (g)	Recovery (%)
Dry-out experiments				
1	290.53	0	2.78	4.8
2	289.70	0	5.61	10.6
Average	290.12	0	4.20	7.7
Partial water-loss experiments				
1	200.21	0.35	14.08	48.5
2	200.32	0.24	12.13	41.6
Average	200.27	0.29	13.11	45.1
Partial water-loss experiments				
1	200.71	1.51	19.45	66.8
2	200.66	2.06	22.25	76.5
Average	200.67	1.78	20.85	71.7
No water-loss experiments				
1	200.33	4.16	25.51	87.8
2	200.60	3.89	24.93	85.7
Average	200.47	4.03	25.22	86.8

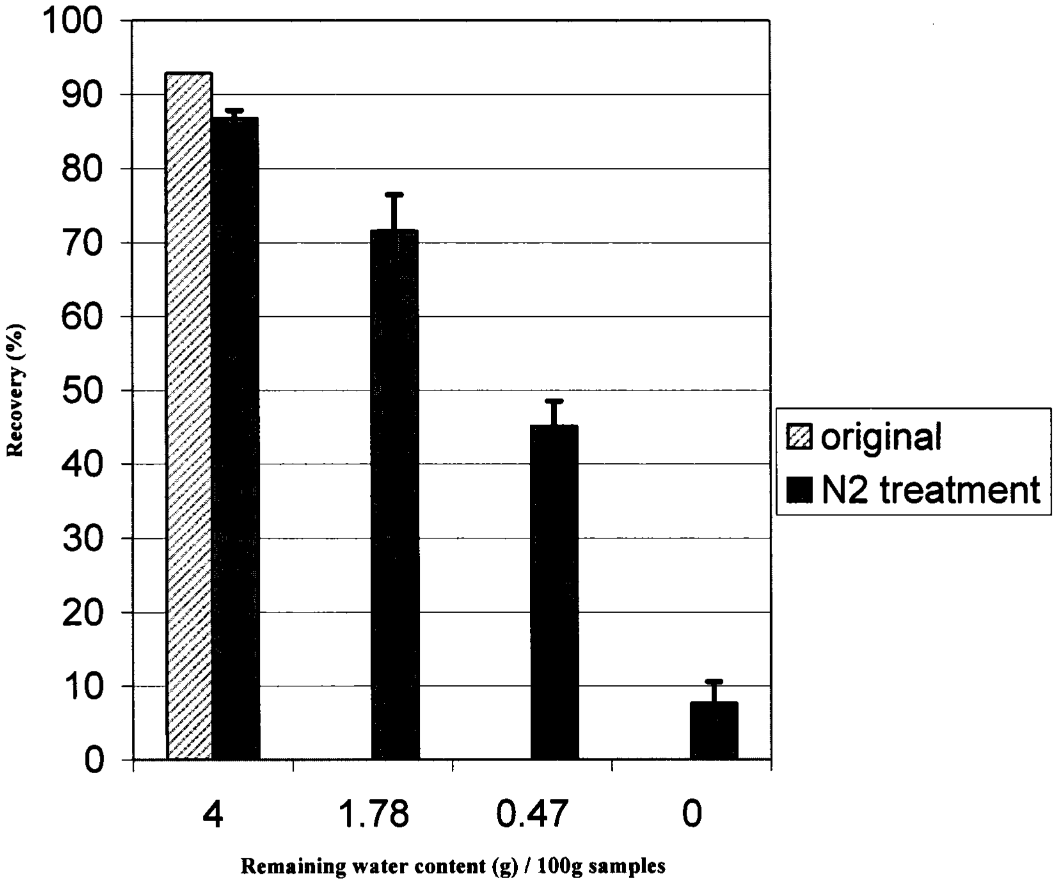

Figure 5-2: Bitumen recovery as a function of the remaining water content by nitrogen treatment

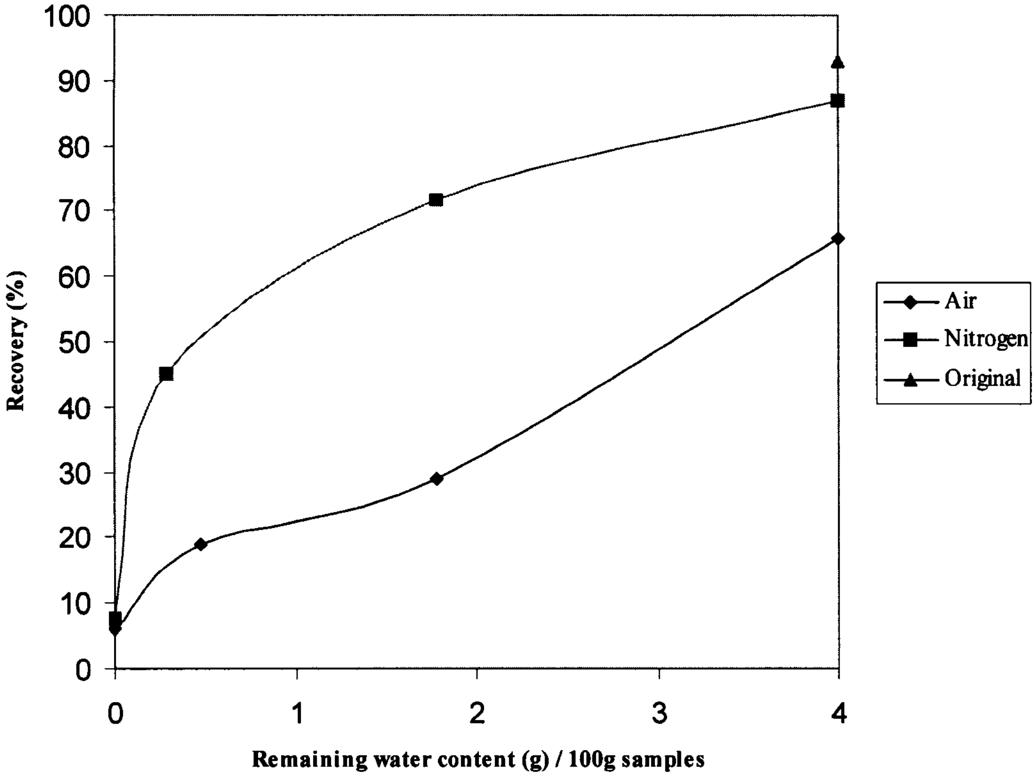

Figure5-3: The recovery differences between air treatment and nitrogen treatment

5.3 Froth Quality

During the oil sand weathering process, not only the recovery decreased, but also the froth quality deteriorated. Another objective of this work was to find out the relationship between the bitumen /solids ratio in the recovered bitumen forth and the remaining water content of the treated oil sands samples.

The test results obtained with samples under air treatment are shown in Table 5-3. The bitumen/solids ratio of recovered froth is very low for the dry-out experiment since the bitumen could not be liberated from the sands grains after the ores were dried out. There was only lean bitumen froth layer formed on the top of the flotation pulp. The froth collected was mainly solids and water with small amounts of bitumen. High bitumen froth quality was obtained in the experiment using samples without water loss. In this case, the bitumen was observed to be liberated and floated to form a thick layer of froth on the top of the flotation pulp. For the partial-water-loss experiment, the froth quality improved with an increase in the remaining water content of the treated ore. Figure 5-4 shows that the bitumen/solids ratio decreases as the remaining water content of the treated sample decreases under air treatment.

The test results under nitrogen treatment are shown in Table 5-4. From the experiments designed for the nitrogen treatment, the same phenomenon as under air treatment was observed. The froth quality is the poorest for the dry-out experiment and the highest for the no-water-loss experiment. The froth quality for the partial-water-loss experiment is between these two extreme situations. Figure 5-5 again shows that the bitumen/solids ratio decreases with decreasing water content remaining in the oil sands sample treated under nitrogen environment. This observation was consistent with what we found in the experiments under air treatment.

Figure 5-6 shows the comparison of the froth quality between air treatment and nitrogen treatment. It is easy to understand that there is little difference in the froth quality between air treatment and nitrogen treatment for the dry-out experiments. When connate water dries out, the bitumen cannot be liberated from sands grains, no matter whether the oil sands sample was treated with air or nitrogen. Bitumen liberation is a prerequisite for bitumen extraction. For the no-water-loss experiments, however, there is a big froth quality difference. The bitumen/solids ratio under the nitrogen treatment is much higher than under air treatment.

The froth quality curve under nitrogen treatment is higher than that under air treatment for a given water loss. This finding suggests that although water-loss definitely plays an important role in froth quality deterioration of weathered oil sands, the oxidation of oil sands also has a significant impact on the bitumen froth quality. Furthermore, although the froth quality obtained from the no-water-loss experiment under nitrogen treatment is much better than that under air treatment, it is far below the froth quality of original untreated oil sands. This tells us that apart from water-loss and oxidation, there are some other factors (e.g. light-end loss during weathering) that affect the froth quality of treated oil sands. This remains an area for further exploration.

Table 5-3: Test results of froth quality for samples after air treatment

Test No.	H_2O content (g /100g sample)	Bitumen in froth (g)	Solids in froth (g)	Bitumen /Solids
Dry-out experiments				
1	0	1.99	19.49	0.10
2	0	1.60	16.05	0.10
Average	0	1.78	17.77	0.10
Partial water-loss experiments				
1	0.31	5.57	26.99	0.21
2	0.62	10.56	23.12	0.46
Average	0.47	8.07	25.01	0.33
Partial water-loss experiments				
1	1.87	9.43	7.08	1.33
2	1.68	7.47	5.22	1.43
Average	1.78	8.45	6.15	1.38
No water-loss experiments				
1	4.01	19.17	5.18	3.70
2	4.01	18.28	6.35	2.88
Average	4.01	18.73	5.77	3.29

Table 5-4: Test results of froth quality for samples after Nitrogen treatment

Test No.	H_2O content (g /100g sample)	Bitumen in Froth (g)	Solids in froth (g)	Bitumen / solids
Dry-out experiments				
1	0	2.78	4.02	0.51
2	0	5.61	8.10	0.55
Average	0	4.20	6.06	0.53
Partial water-loss experiments				
1	0.31	13.48	4.42	3.05
2	0.25	12.23	4.18	2.93
Average	0.25	12.86	4.30	2.99
Partial water-loss experiments				
1	1.51	19.45	2.79	6.97
2	2.06	22.25	2.86	7.78
Average	1.78	20.85	2.83	7.38
No water-loss experiments				
1	4.16	25.51	2.51	10.16
2	3.89	24.93	1.73	14.41
Average	4.03	25.22	2.12	12.29

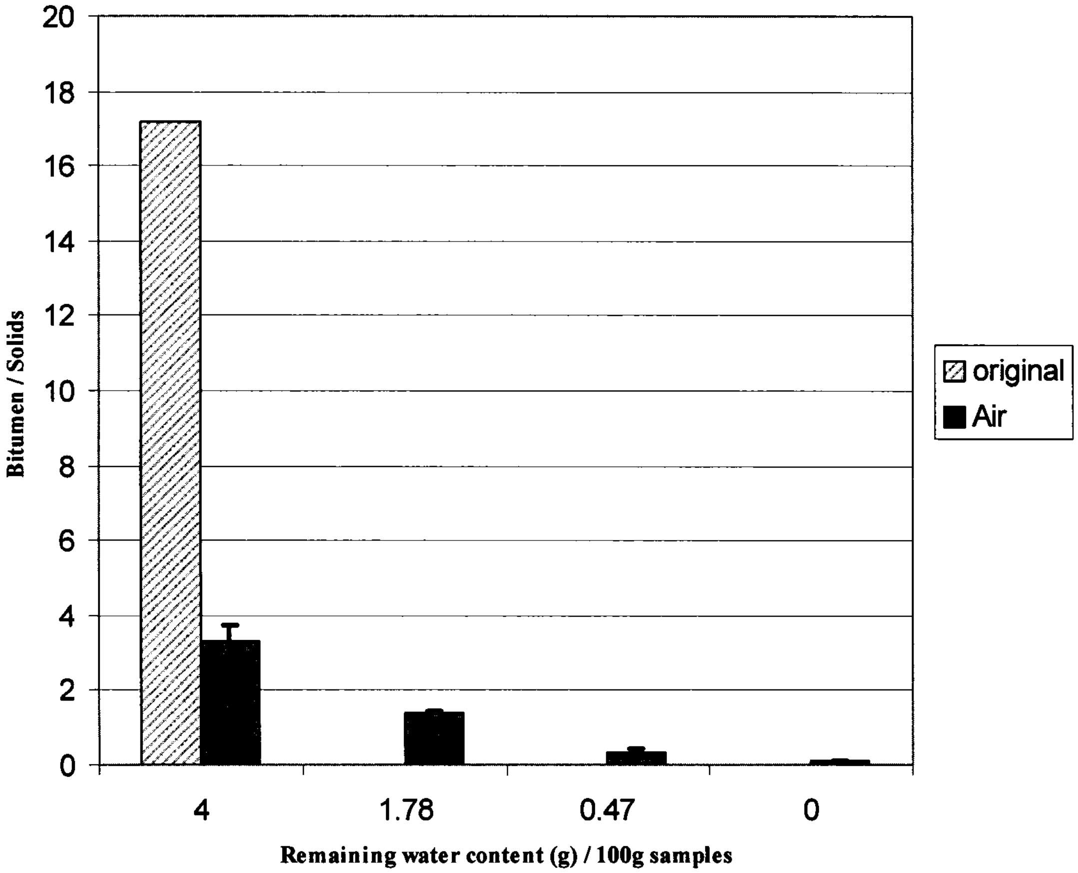

Figure 5-4: Bitumen-solids ratio as a function of the remaining water content by air treatment

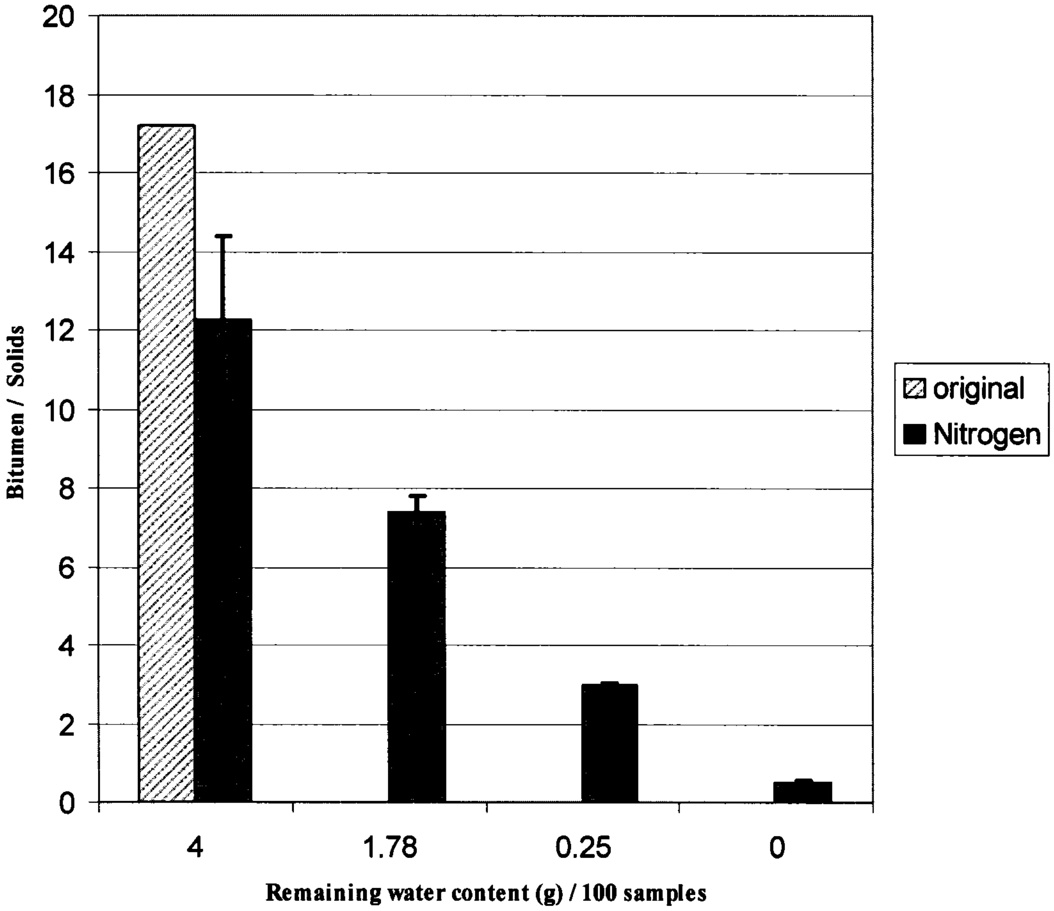

Figure 5-5: Bitumen-solids ratio as a function of the remaining water content by nitrogen treatment

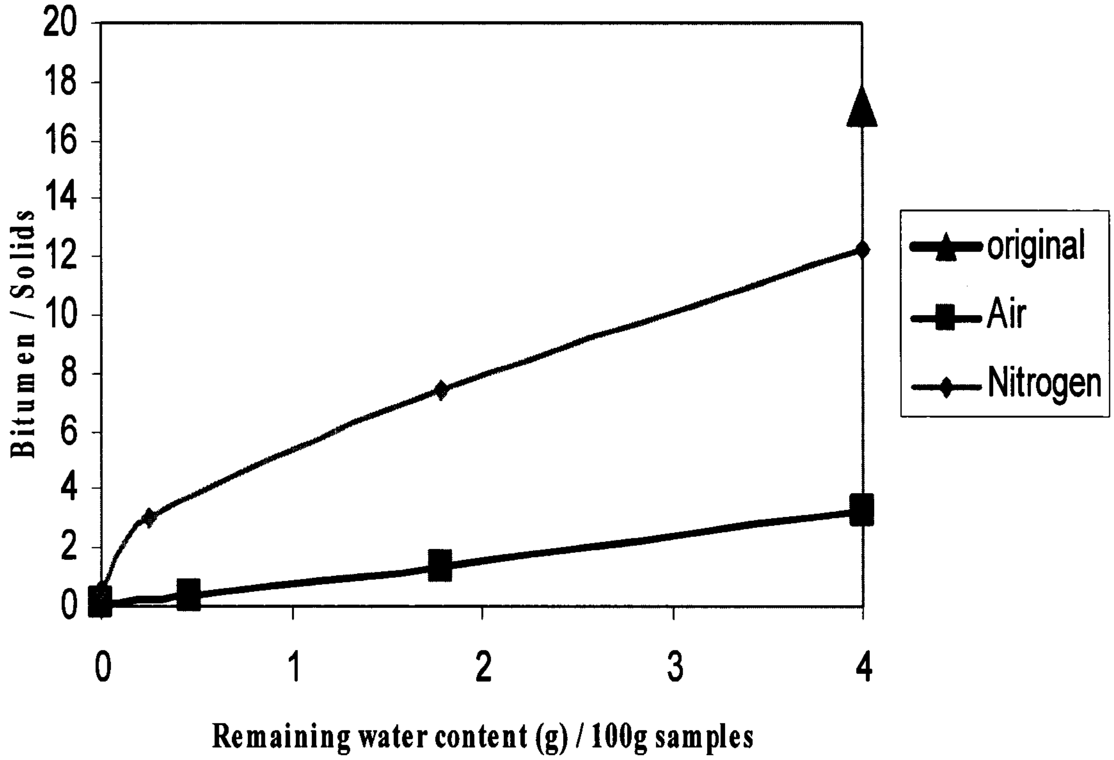

Figure 5-6: Difference in froth quality between samples after air and nitrogen treatment, respectively

5.4 The Hydrophobicity of Oil Sands Solids

It is well known that the hydrophobic solids will stay in an oil phase and hydrophilic solids will stay in an aqueous phase if the solids are placed into an oil / water two-phase system. Based on this principle, this experiment was designed to test if the hydrophobicity of solids changes when the oil sands samples are weathered.

It is observed that the solids from original untreated oil sands samples stay in the water phase as shown in Figure 5-7. There are some humic materials with a few solids hanging near the interface between oil and water. It can be concluded that the solids extracted from original oil sands samples are almost all hydrophilic.

5.4.1 Experiments under air treatment

As shown in Figure 5-8, for the no-water-loss experiment, majority of the solids extracted from the treated ores stays in the water phase. These solids are, therefore, hydrophilic. The materials hanging near the interface between oil and water are humic with a few solids. However, for the partial-water-loss experiment (part of the connate water are evaporated during treatment), only some of the solids extracted from treated ores stay in the water phase while others attach to the oil droplets, staying in the oil phase and becoming hydrophobic. For the dry-out experiments, almost all the solids stay in the oil phase and become hydrophobic. This finding is quite reasonable to explain the bitumen recovery results. The solids extracted from treated ores without water loss remain hydrophilic and the water film remains intact during the treatment. Bitumen is easily liberated from the sand grains leading to the highest recovery as anticipated. For the partial-water-loss experiment, some solids become hydrophobic and will attach to the bitumen directly. Therefore the liberation of this part of bitumen is difficult leading to a reduced bitumen recovery. The dry-out experiment has the lowest recovery since almost all of the solids are hydrophobic. The water film inside the oil sands structure is completely destroyed. Bitumen attaches to sand grains directly. It is impractical to process the oil-wet oilsands using hot-water technology.

5.4.2 Experiment under nitrogen treatment

As shown in Figure 5-9, for the no-water-loss experiment, almost all of the solids extracted from the treated ores stay in the water phase and are thus hydrophilic. For the partial-water-loss experiment, some solids stay in the water phase and are hydrophilic while others attach to the oil droplets, staying in the oil phase because of being hydrophobic. For the dry-out experiments, almost all the solids become hydrophobic and stay in the oil phase.

It is evident that the same weathering phenomenon is observed under nitrogen treatment as under air treatment. The higher the connate water loss during the treatment, the more likely it is that most of the solids will stay in the oil phase.

Figures 5-10 and 11 show that the solids extracted from the flotation tailing one day after flotation are almost all hydrophilic, no matter how the oil sand ores were treated.

The results from quantitative analysis for the solids hydrophobicity are shown in Table 5-5. When there is no water loss during treatment, 97.6 percent of the solids extracted from treated ores are hydrophilic. As the connate water contents of treated ores drop to 1.78 and 0.20 (g/100g treated ores), the percentages of hydrophilic solids drop to 84.1 and 22.0% respectively. When the connate water of treated ores is completely evaporated, only 5.8 percent of solids are hydrophilic. For the air treatment of oil sands ores, 93.4 percent of the solids extracted from treated ores are hydrophilic when there is no water loss during treatment. The percent of the hydrophilic solids is 28.4 and 4.6 when the connate water contents of treated ores are 1.78 and almost zero.

Figure 5-12 show that the percentages of the hydrophilic solids extracted from the treated ores decrease with decreasing remaining water contents, more pronounced with air treatment.

Figure 5-13 shows that for a given treatment condition, i.e. air vs. nitrogen, the bitumen recovery is closely related to the percentage of hydrophilic solids. With a higher percentage of hydrophilic solids in the treated ores, higher recovery is obtained. Under the same percentage of hydrophilic solids, the recoveries of the ores under nitrogen treatment are higher than that under air treatment.

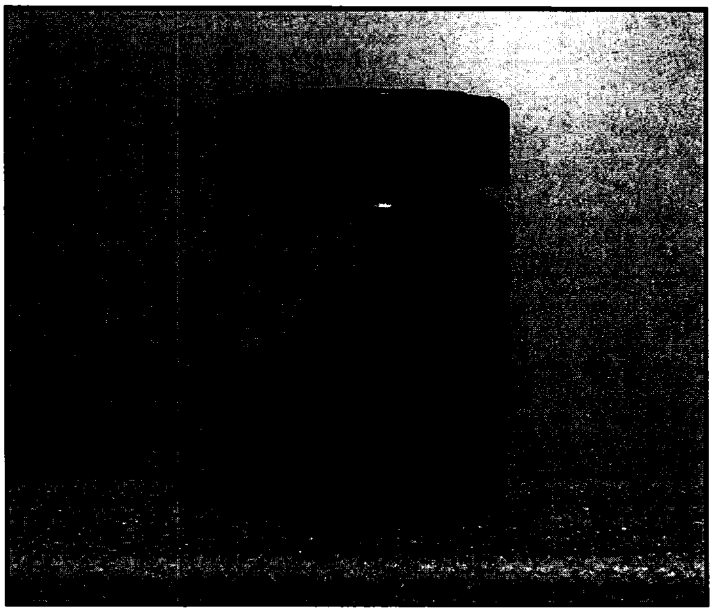

Figure 5-7: Photograph of the hydrophobicity of the solids from the original ore

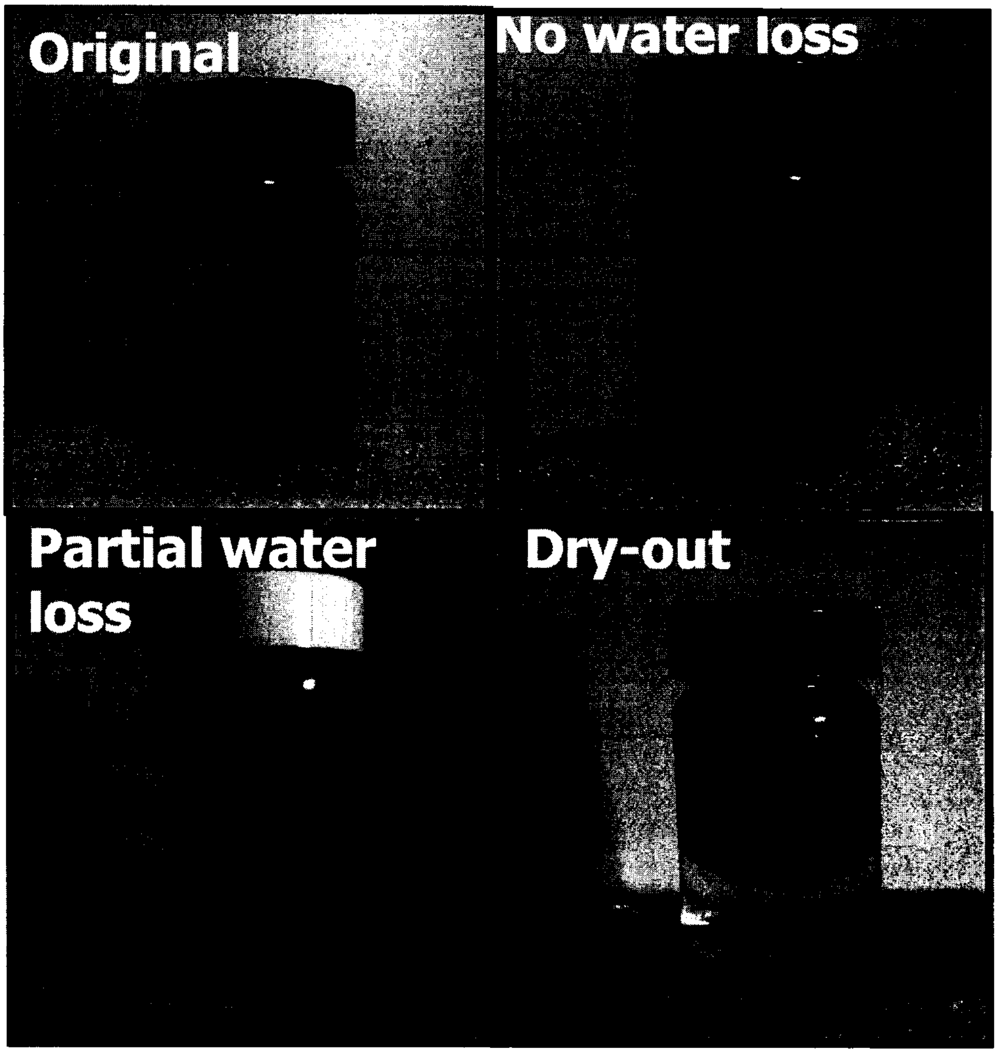

Figure 5-8: Photograph of the hydrophobicity of the solids from the ores under air treatment

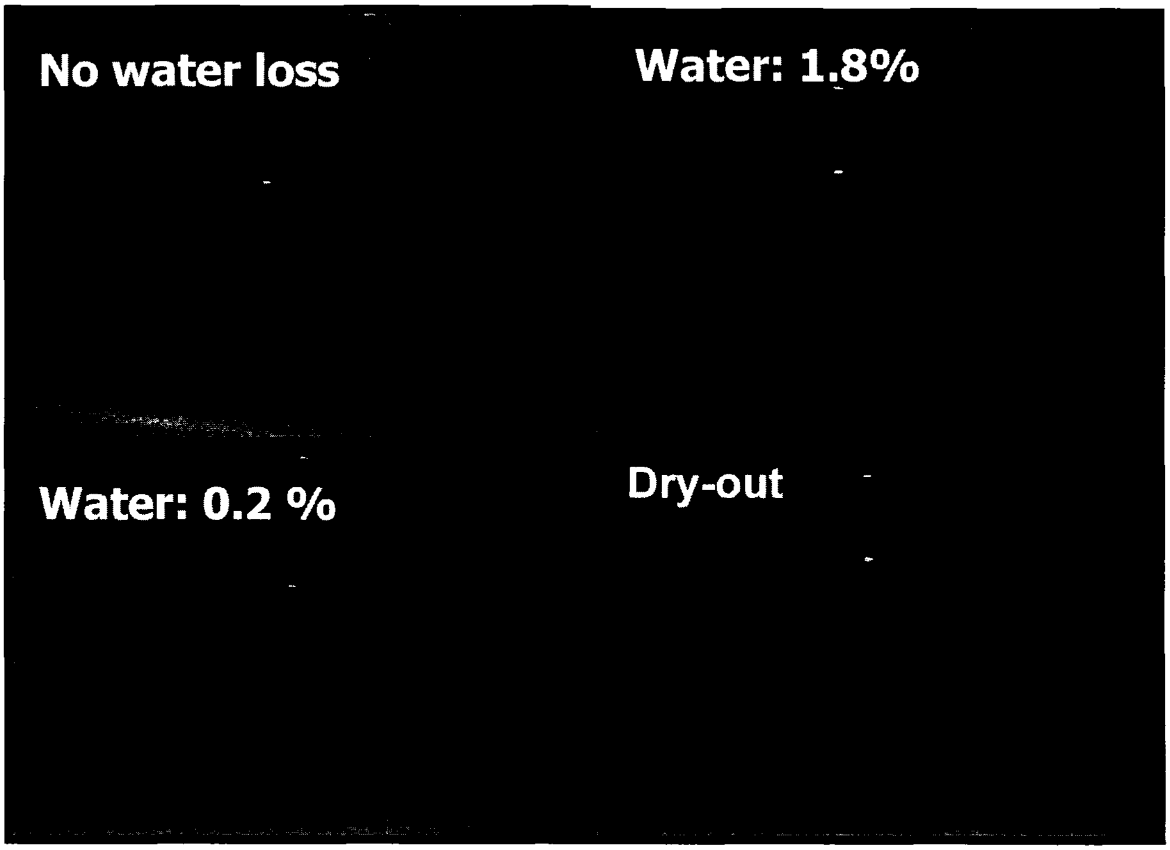

Figure 5-9: Photograph of the hydrophobicity of solids from the ores under nitrogen treatment

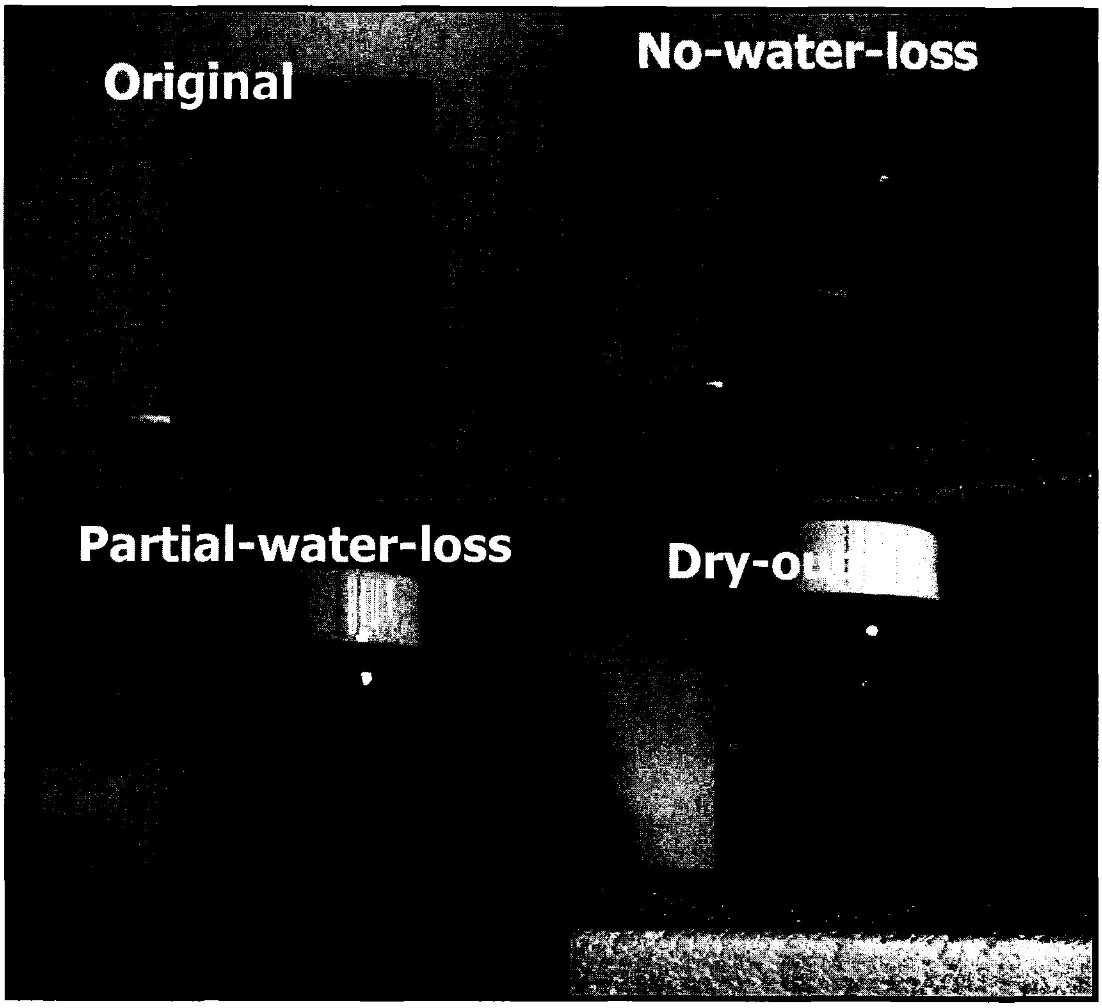

Figure 5-10:Photograph of the hydrophobicity of the solids from the tailings under air treatment

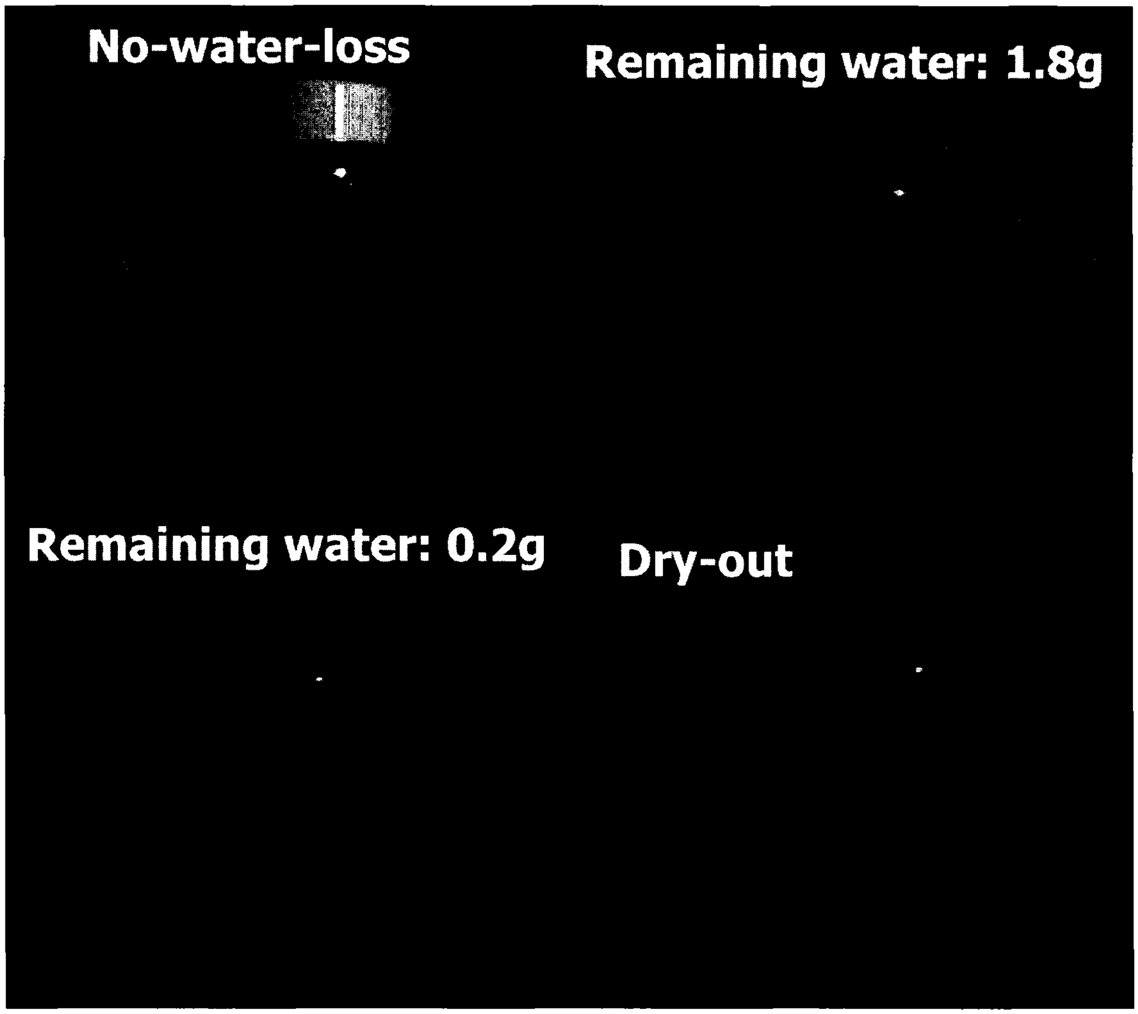

Figure 5-11: Photograph of the hydrophobicity of the solids from the tailings under nitrogen treatment

Table 5-5: The results of solids hydrophobicity tests

	Water content (g)	Sample wt. (g)	Solids in water (g)	Hydrophilic solids (%)
Nitrogen treatment				
Test 1	0	2.64	0.18	6.8
Test 2		2.77	0.13	4.8
Average		2.71	0.16	5.8
Test 1	0.2	2.61	0.53	20.2
Test 2		2.57	0.61	23.7
Average		2.59	0.57	22.0
Test 1	1.78	2.67	2.30	86.1
Test 2		2.76	2.27	82.1
Average		2.72	2.29	84.1
Test 1	4.0	2.58	2.52	97.5
Test 2		2.91	2.84	97.7
Average		2.75	2.68	97.6
Air treatment				
Test 1	0	2.37	0.08	3.37
Test 2		2.58	0.15	5.80
Average		2.48	0.12	4.59
Test 1	1.78	2.86	0.72	25.16
Test 2		2.79	0.88	31.56
Average		2.83	0.80	28.36
Test 1	4	2.83	2.65	93.79
Test 2		2.57	2.39	93.00
Average		2.70	2.52	93.39

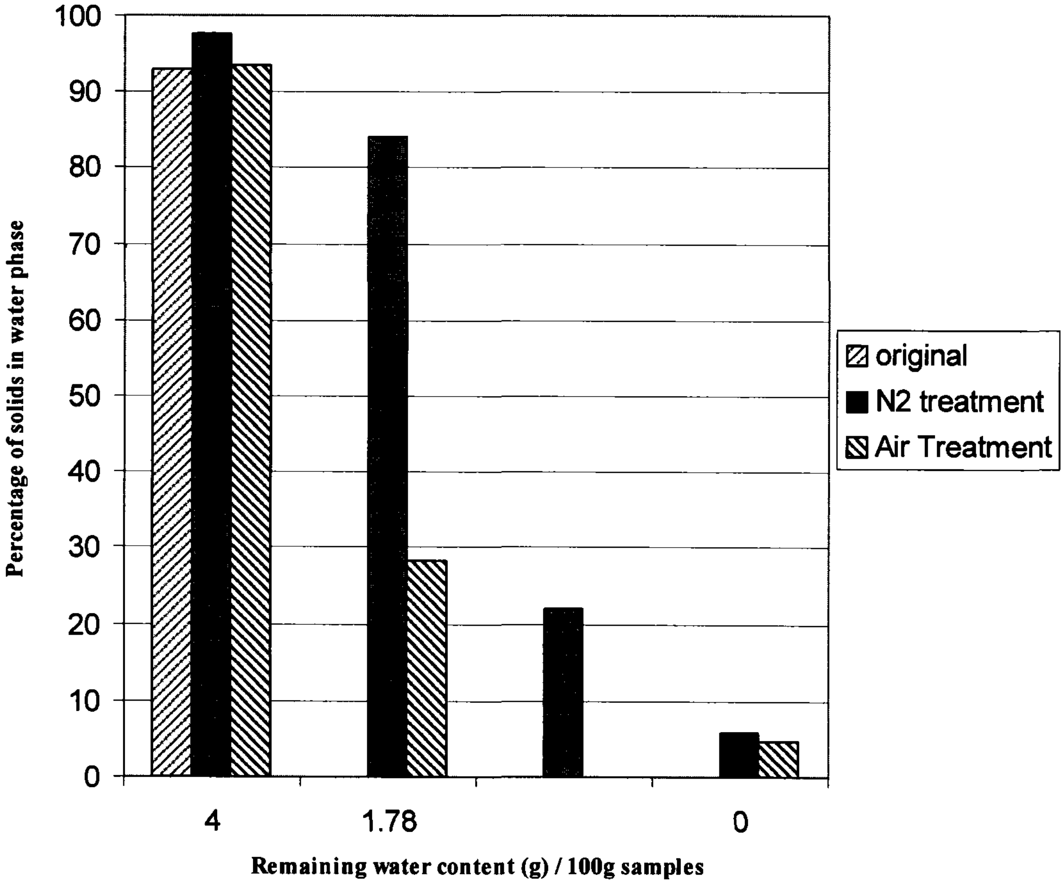

Figure 5-12: Quantitative analysis of solids hydrophobicity

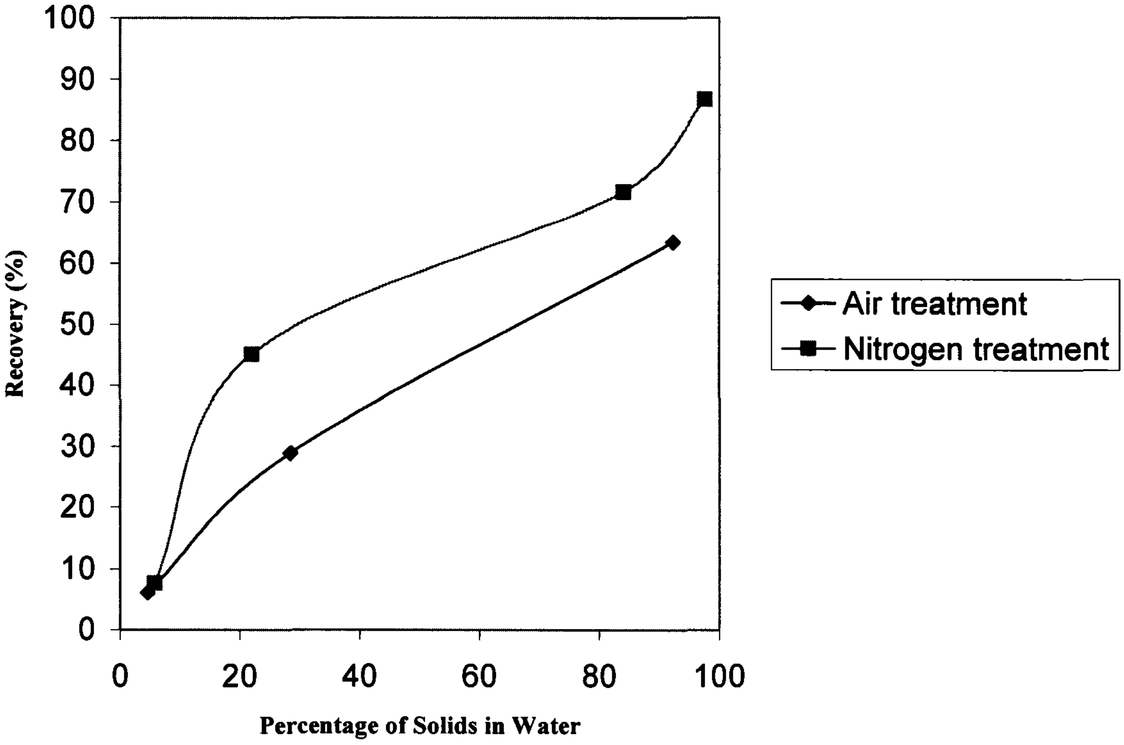

Figure 5-13: Recovery as a function of percentage of solids in water

5.5 Reversibility of Oil Sands Weathering

In the hydrophobicity study, it was found that the solids extracted from the treated ore with controlled water loss change from hydrophilic to hydrophobic, depending on the degree of water loss. It would be interesting to note whether the solids could become hydrophilic again when the treated samples were immersed into water. This study will investigate the reversibility of oil sands weathering by immersing the weathered ores under air treatment into water for a given period of time.

The test results are shown in Table 5-6. Figure 5-13 shows that the processability improves with increasing immersion time until the recovery reaches a peak. This finding suggests that oil sands weathering could be reversible. After one day, the recovery decreases with increasing immersion time. This decrease could be attributed to the oxidation of the treated ores.

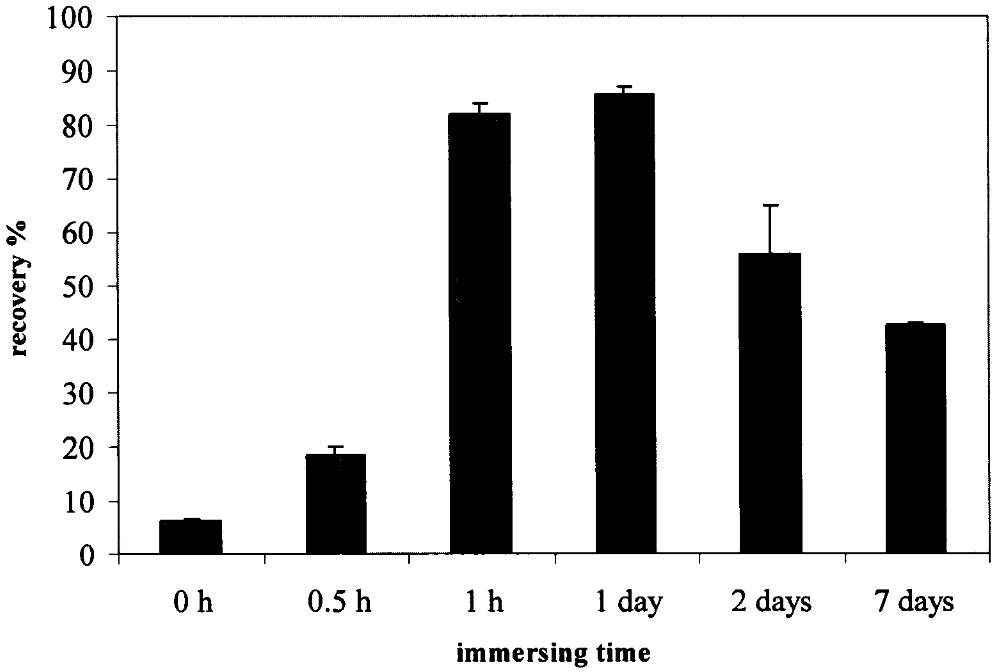

Figure 5-15: The reversibility study of oil sands weathering

Table 5-6: Reversibility study of oil sands weathering

	Immersed time	Sample wt. (g)	Bitumen (g)	Recovery (%)
Test 1	0.5 hour	200.5	5.83	20.1
Test 2		200.6	4.96	17.1
Average		200.2	5.40	18.6
Test 1	1 hour	200.2	23.23	80.0
Test 2		200.6	24.01	83.9
Average		200.4	23.62	82.0
Test 1	1 day	200.4	25.35	87.2
Test 2		200.4	24.42	84.0
Average		200.4	24.89	85.6
Test 1	2 days	200.7	9.61	47.0
Test 2		200.5	18.8	64.6
Average		200.6	14.21	55.8
Test 1	7 days	201.6	12.59	43.1
Test 2		200.7	12.32	42.3
Average		201.2	12.46	42.7

5.6 Tailings and Bitumen Contact Angle Analysis

The tailings water is analyzed in this study to investigate if the pH, calcium, or magnesium contents change during oil sands weathering. The surface tension of tailings water is also measured to investigate whether additional surfactant is produced or not by weathering. All of the water chemistry analysis of the tailings, except for the pH value, was analyzed by Merali, a technician in our department. An Atomic Adsorption Spectrophotometer was used to determine Ca and Mg levels. The test results are shown in Table 5-7. There is no clear trend observed. However, the surface tension of tailing water after air treatment is lower than that after nitrogen treatment, indicating a higher release of surfactant species from bitumen oxidized in air.

The contact angles between bitumen and water in air are also measured using a Drop Shape Analysis System (DSA10). The results are shown in Table 5-8.There are no big differences in contact angles between bitumen and water during oil sands weathering. This finding suggests that the impact of weathering on bitumen hydrophobicity is negligible. The bitumen after weathering remains hydrophobic with contact angles around 90°.

Table 5- 7: Results of the tailings water chemistry analysis

Remaining water content (g / 100g sample)	Ca^{2+} in tailings (ppm)	Mg^{2+} in tailings (ppm)	Fe^{2+} in tailings (ppm)	pH of the tailings water	Surface tension of the tailing water (mN/M)
Original (4)	0.2	0.45	0.4	6.79	71.4
Air treatment experiments					
0	0.9	0.81	0.1	7.18	65.34
1.8	0.5	0.57	<0.1	6.63	66.77
4	0.3	0.52	<0.1	6.62	65.87
Nitrogen treatment experiments					
0	1.2	1.03	<0.1	6.44	67.19
0.25	0.1	0.37	0.4	5.96	70.54
1.78	0.8	0.62	<0.1	7.01	72.41
4	0.4	0.59	0.3	7.03	72.08

Table 5-8: Results of the contact angle tests

Remaining water content (g / 100g sample)	Contact angle (°)	Experiment
0	87.4	Air treatment
4	91.6	Air treatment
	91.4	Nitrogen treatment
	90.2	Original, untreated

5.7 Weathering Phenomenon Using Process Water

De-ionized water provides a very good working platform for an oil sand weathering study. However, using process water to confirm some of the findings observed in de-ionized water is necessary for this study to make link between fundamental study and industrial practice. The process water used for this study was from Syncrude. Its content of various species is given in the table below.

Table 5-9: the contents of species in the process water

Ca (mg/L)	Mg (mg/L)	pH	K (mg/L)	Na (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)
48	19	8.3	14.3	503.0	431.0	1.5	63.1	647.0

All the experiments for recovery and froth quality of flotation using ores after air treatment are repeated using the process water. The test results are shown in Tables 5-10 and 5-11. Figure 5-15 clearly shows that the recovery decreases with decreasing remaining water content of the ores treated, which is consistent with the results obtained using de-ionized water. In other words, no matter what kind of water is used, the lower the remaining water is in the treated ore, the poorer the processability of the treated ores will be. Figure 5- 15 shows that the bitumen/solids ratio also decreases with decreasing remaining water content of treated ores, as also observed using de-ionized water.

However, the processability of treated ores using process water is better than using de-ionized water, as shown in Figure 5-16. As we know that a higher pH value can reduce the interfacial tension between bitumen and solids, resulting in a better liberation value (8.3) of the process water is higher than that of the de-ionized water, using process water can enhance the bitumen recovery of the treated oil sands. Figure 5-17 shows that for the original ore, the froth quality obtained using de-ionized water is much better than using process water. But the process water did enhance the froth quality of treated oil sands samples.

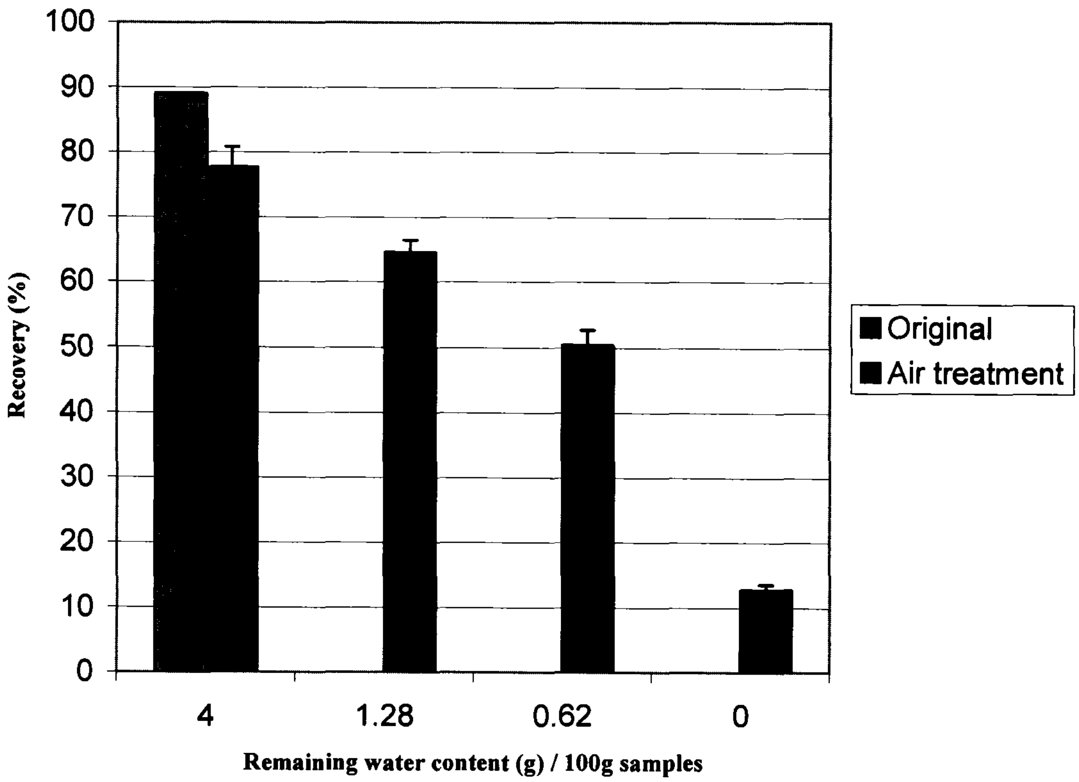

Figure 5-15: Recovery as a function of the remaining water content of treated ores by using process water

Table 5-10: Results of recovery tests by using process water

	Sample wt. (g)	H_2O content (g /100g sample)	Bitumen in froth (g)	Recovery (%)
Dry-out experiments				
Test 1	200.9	0	3.97	13.6
Test 2	200.8	0	3.50	12.0
Average	200.9	0	3.74	12.8
Partial water-loss experiments				
Test 1	200.66	0.63	15.35	52.7
Test 2	201.89	0.60	14.09	48.1
Average	201.28	0.62	14.72	50.4
Partial water-loss experiments				
Test 1	202.12	1.35	19.47	66.43
Test 2	201.63	1.21	18.27	62.49
Average	201.86	1.28	18.87	64.46
No water-loss experiments				
Test 1	200.48	3.60	21.69	74.6
Test 2	200.09	4.10	23.46	80.8
Average	200.29	3.85	22.58	77.7
Untreated original ore				
Test 1	200.52	Untreated	26.09	89.7
Test 2	200.49	Untreated	25.91	89.1
Average	200.51		26.00	89.4

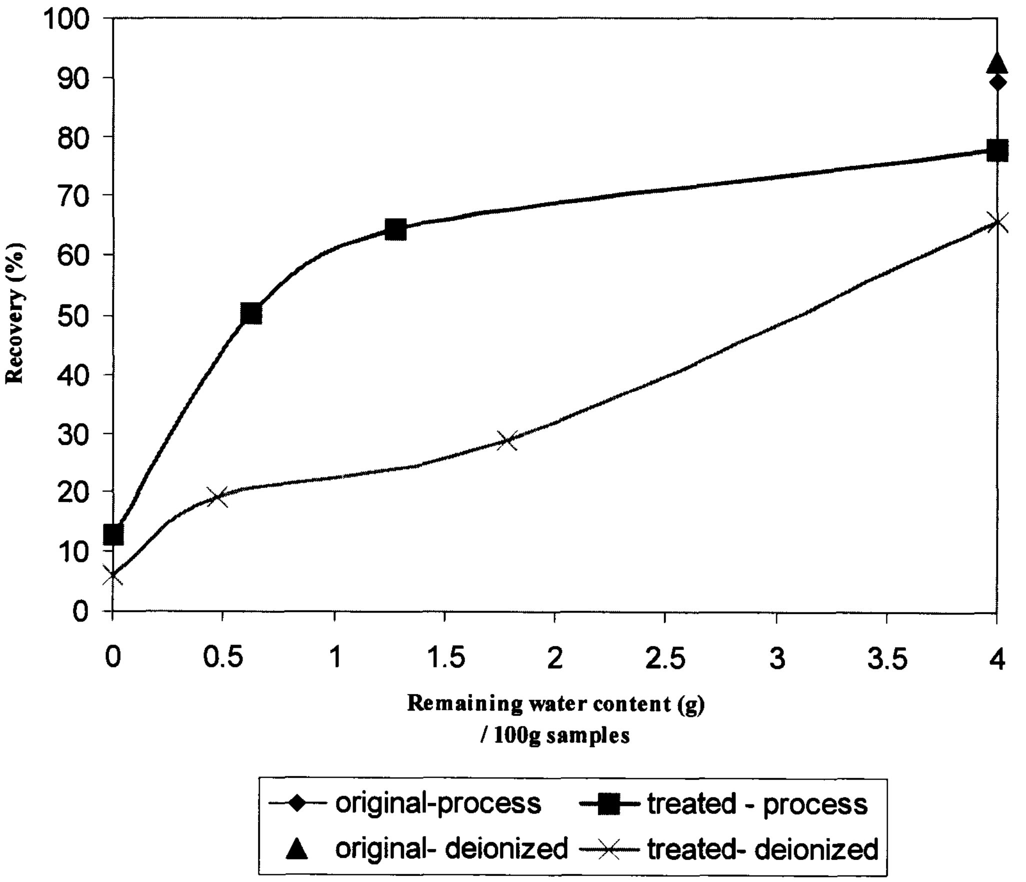

Figure 5-16: Recovery differences between using process water and de- ionized water under air treatment

Table 5-11: Results of froth quality tests by using process water

	H_2O content (g /100g sample)	Bitumen in froth (g)	Solids in froth (g)	Bitumen / Solids
Dry-out experiments				
Test 1	0	3.97	11.58	0.34
Test 2	0	3.50	10.57	0.33
Average	0	3.74	11.08	0.33
Partial water-loss experiments				
Test 1	0.63	15.35	5.84	2.63
Test 2	0.60	14.09	7.37	1.91
Average	0.62	14.72	6.61	2.27
Partial water-loss experiments				
Test 1	1.35	19.47	5.15	3.78
Test 2	1.21	18.27	5.94	3.08
Average	1.28	18.87	5.55	3.43
No water-loss experiments				
Test 1	3.60	21.69	4.94	4.39
Test 2	4.10	23.46	4.82	4.87
Average	3.85	22.58	4.88	4.62
Untreated original ore				
Test 1	untreated	26.09	2.67	9.51
Test 2	untreated	25.91	2.59	9.91
Average		26.00	2.63	9.71

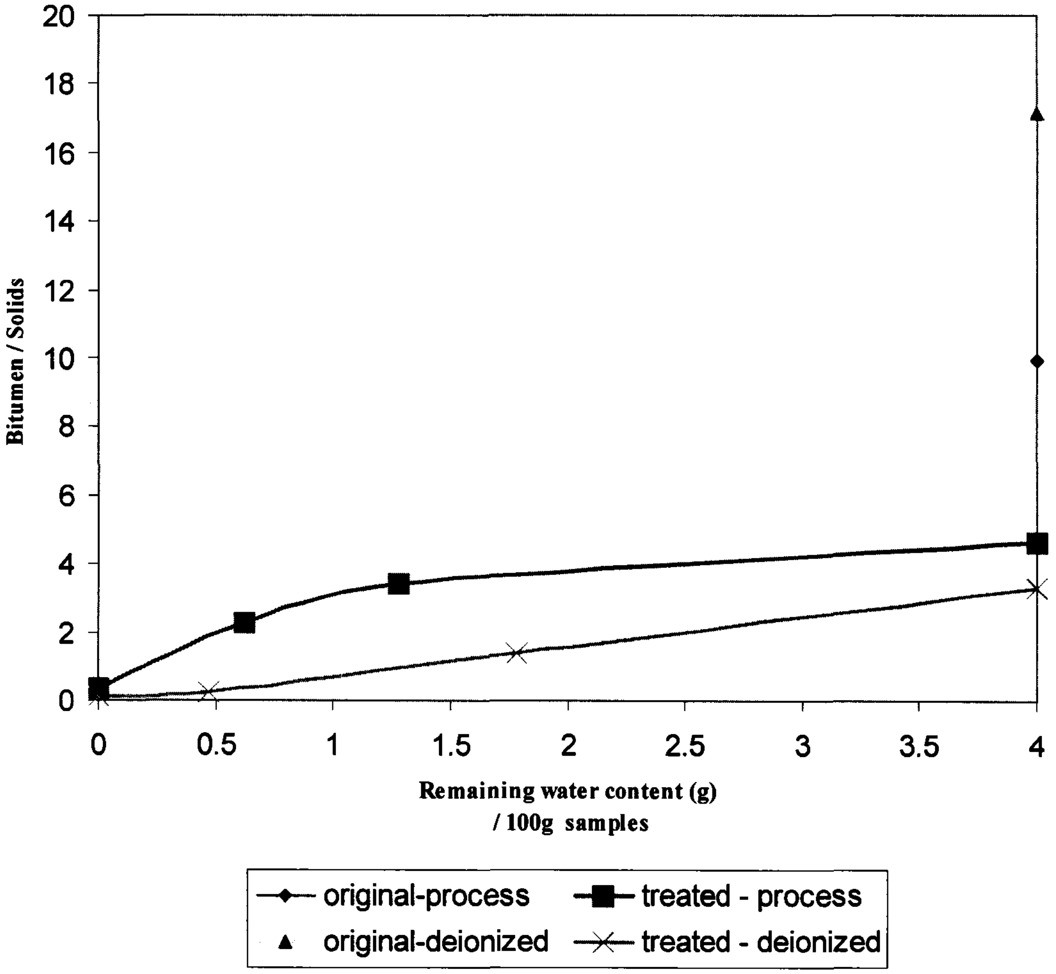

Figure 5-17: Froth quality obtained using process water and de-ionized water with ores samples after air treatment

Chapter 6: Conclusion

In this study, a series of techniques have been proposed and investigated. These techniques included oil sands weathering inside an oven, both under air nitrogen environment, and evaluation of solid hydrophobicity. Through the experiments, the following conclusions are drawn:

- Oil sands can be naturally weathered. Bitumen recovery of weathered oil sands decreases and the forth quality deteriorates with weathering time. Oil sands weathering can be confirmed by artificially treating oil sands ores in an oven at controlled temperature and environment.
- The water-loss from the weathered oil sands plays an important role in oil sands weathering. When the remaining water contents of weathered oil sands decreases, the recovery decreases and the froth quality deteriorates.
- The processability of treated ores under a nitrogen environment is better than that in air. The froth quality of ores treated under nitrogen is higher than in air, except for the totally desiccated ores. This finding suggests that oxidation may also play a role in oil sands weathering.
- The hydrophobicity of solids obtained from weathered oil sands can change as a result of water-loss during oil sand weathering. The solids extracted from original ore and from treated ores without connate water loss are almost all hydrophilic. Some solids become hydrophobic when treated ores start to lose the connate water. Almost all the solids extracted from the totally desiccated oil sands ores are hydrophobic.

- The weathering process is, to an extent, reversible. Immersing totally desiccated oil sands ores into water for a certain time can enhance their processability.
- Oil sand weathering has no impact on the contact angle between bitumen and water in air.
- Oil sands weathering has a marginal impact on the surface tension of the tailings water.

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