

University of Alberta

**OIL SANDS SOLIDS WETTABILITY AND ITS RELATION TO OIL SANDS
PROCESSABILITY**

by

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the requirements for the degree of **Master of Science**.

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Abstract

One of the major steps in the extraction of bitumen from oil sands using the Clark Hot Water Extraction process is the liberation of bitumen from sand grains. In this study, flotation tests were performed to determine the processability of different oil sands ores and to isolate the solids from the oil sands. A jar shaking test was developed to quickly estimate the processability of the oil sand ores. The wettability of coarse solids (-250 +106 μm) and fine solids (-45 μm) was determined separately. The wettability of the coarse solids was measured by using a film flotation technique and an oil-water partitioning test. Coarse solids washed with both ethanol and toluene were less hydrophobic compared to those washed with ethanol or toluene alone, and drying increased the hydrophobicity of the coarse solids. The coarse solids washed with ethanol after drying were more hydrophobic than those washed with ethanol before drying. A water drop penetration test and an initial contact angle measurement were used to characterize the wettability of the fine solids. The wettability of the solids extracted from oil sands correlates well with the processability or bitumen recovery. In general, the more hydrophobic the solids are the poorer, the processability of oil sands ore.

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I dedicate this thesis to my parents, my family and Mini Goyal

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Nomenclature

CHWE	Clark Hot Water Extraction
BEU	Batch Extraction Unit
PSV	Primary Separation Vessel
TMW	Tailing and Middling Water
WWWC	Wet Water Washed Coarse
WEWC	Wet Ethanol Washed Course
DTWC	Dry Toluene Washed Coarse
DEWC	Dry Ethanol Wahsed Coarse
DETWC	Dry Ethanol Toluene Washed Coarse
XPS	X-ray Photoelectron Spectroscopy

Chapter 1

Introduction

1.1 Oil Sands Mining and Extraction

Oil sands are unconsolidated sand deposits impregnated with high molar mass viscous petroleum, normally referred to as bitumen. Oil sands are found throughout the world, and the largest deposit exists in the Athabasca of Alberta, Canada. The Athabasca region's oil sands deposit has an estimated in place reserve of 869 billion barrels of bitumen with an estimated 60 billion barrels recoverable by using surface mining methods. This region covers approximately 46800 square kilometers [4]. The oil sand deposits in Alberta occur in four major geographical areas: Athabasca, Wabasca, Peace River and Cold Lake. The average bitumen saturation by weight is more than 10% in these areas. The near surface oil sand deposits in the Fort McMurray area have enabled the deposit to be recovered by surface mining techniques. In fact, oil sands processing is one of the fastest-growing industries in Alberta [15]. The recent high world crude oil prices have encouraged many new industrial ventures to invest for recovering bitumen from the oil sands of northern Alberta and then upgrading the bitumen into useful petroleum and fuel products.

The current bitumen separation processes for surface-mined oil sands are based on the hot water extraction process (HWEP) [3]. The hot water extraction process takes advantage of the fact that the solids from oil sands are hydrophilic. In this process, Ores are mixed with hot water. Hot water increases the temperature of the bitumen, hence lowering its density and viscosity. Air is also used to further reduces the density by bubbles attaching to the bitumen assisting in separation of solids and bitumen in a separation vessel.

At present, the three major players in bitumen production from oil sands are Suncor Energy Inc., Syncrude Canada Ltd. and Albian Sands Energy Inc. All three produces use similar methods to extract bitumen from oil sands. The basic units of bitumen production consist of mining, extraction and upgrading. Only through proper integration of all these basic units can sustainable bitumen production be achieved.

Mining

The oil sands are mined using large shovels and trucks. Mining starts with the removal of overburden materials, which can be as much as 40 m thick. Once the overburden is removed, the oil sand ores become accessible. The thickness of oil sand deposits can vary from 20 to 90 m. In order for open pit mining to be economical, the stripping ratio should be much less than two [21]. Oil sand ore is mined using both hydraulic as well as electric (or cable) shovels. The ore is transported from the mine site to crushers by using high-payload-capacity trucks. Their payload can be as high as 400 tonnes.

Extraction

The crushed ore is mixed with process water using a combination of a mixing box, stirred tanks, cyclo feeder, or rotary breakers. Initial bitumen liberation as well as aeration of bitumen take place when the ore is mixed with process water. The slurry is then transported to the Primary Separation Vessel (PSV) by hydrotransport pipelines where major bitumen liberation from the sand grains, aeration and bitumen-bitumen coalescence take place. Gravity separation takes place in the PSV where the bitumen floats to the top by attaching to or engulfing air bubbles, and the coarse solids settle to the bottom. The middling slurry contains un-recovered bitumen, which is recovered by a conventional flotation process. The rich froth normally contains 60% bitumen, and 10% solids, with the remaining 30% being water. The froth is further processed to decrease the solids and water. The froth is first de-aerated, and then solvent is added to decrease the froth viscosity. This process helps to remove the solids and water from the de-aerated froth. Incline plate settlers, cyclones, and centrifuges use gravity and centrifugal force to separate heavier materials as underflow

and lighter materials as overflow. Syncrude and Suncor use naphtha as a solvent to decrease the bitumen viscosity, whereas at Albion, paraffinic diluent is used for froth processing. Paraffinic diluent not only decreases the viscosity of bitumen froth but also precipitates the asphaltene. Asphaltene flocculates/coagulates the water and solids, thus producing cleaner bitumen. The use of paraffins (hexane) in froth treatment has its own challenges. Tailings from the bottom PSV and flotation cells are discharged into the tailings ponds. The clean froth is sent to the upgrader for further processing.

1.2 Fundamentals of Extraction

Fundamentally, the bitumen recovery from oil sands using water-based extraction processes involves the following steps [21]:

1. **Lump-size reduction:** lump-size reduction or lump ablation takes place in tumblers or hydrotransport pipelines where the heated outer lump surface is sheared away from the lump.
2. **Bitumen liberation:** bitumen liberation or separation takes place from sand grains. The rate of bitumen liberation depends on the balance between the forces pulling the bitumen away from the sand grains and the forces of bitumen adhering to these grains.
3. **Bitumen bubble attachment:** the density of the liberated bitumen globule is approximately equal to water, so this globule can not float to the top of the PSV or flotation cell by itself. The slurry needs to be aerated. Aeration is achieved by introducing bubbles into the slurry system. The disengaged bitumen from the sand grains attaches to the available air bubbles. The aerated bitumen floats, due to the buoyancy effects, to the top of the gravity separation vessel or flotation cell and is subsequently recovered as a bitumen froth.

Bitumen Liberation

Clearly, bitumen liberation from the sand grains is a major step in the extraction of bitumen from oil sands. How strongly the bitumen adheres to the surface of the solids

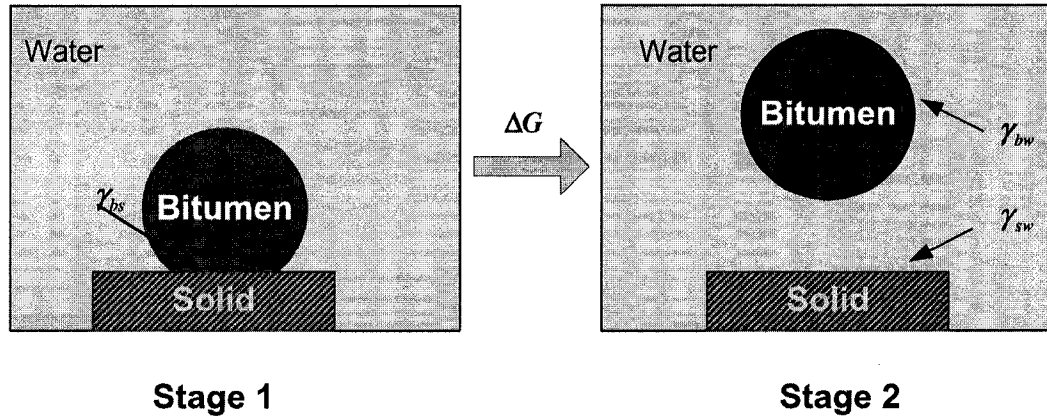


Figure 1.1: Steps involved in bitumen detachment from sand grains (solids)

governs the recovery of bitumen. Figure 1.1 shows a simplified picture of bitumen detachment from the sand grains. The energy required to detach bitumen from sand grains is expressed in terms of free energy per unit area ΔG . The bitumen liberation process involves three different interfaces: the water-solids interface, solids-bitumen interface and bitumen-water interface:

$$\Delta G = \gamma_{bw} + \gamma_{sw} - \gamma_{bs}, \quad (1.1)$$

where ΔG is the free energy per unit area (J/m^2); γ_{bw} is the interfacial free energy of the bitumen-water (J/m^2); γ_{sw} is the interfacial free energy of the water-solids interface (J/m^2) and γ_{bs} is the interfacial free energy of the bitumen-solids (J/m^2).

Equation 1.1 indicates that if the interfacial energy between the bitumen and solids decreases, the energy required to liberate the bitumen from the solids will increase, hence leading to a decrease in overall bitumen release. When the surface of the solids are hydrophobic, the affinity of solids for bitumen increases. This result leads to a decreased interfacial energy between the bitumen and solids, and thus an increase in the energy required to liberate the bitumen.

Bitumen-Bubble Attachment

The attachment of an air bubble to solid particles is governed by the wettability of the particles. If the particles become hydrophobic, then the chance of particles reporting to the froth increases. This result may or may not be desired for the process. Bitumen

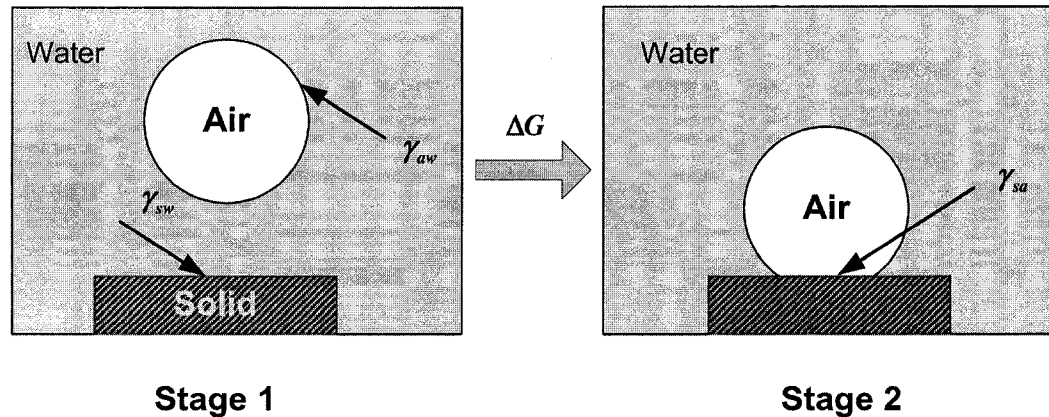


Figure 1.2: Steps involved in air bubble attachment to sand grains (solids)

is inherently hydrophobic in nature, so it gets attached to the air bubbles, but the slurry also contains fines and solids, which can also get attached to the bubbles and then report to the froth.

Once the bitumen is liberated from the sand grains, it needs to attach to the air bubbles so that it can float to the top of the PSV. Some fines can also get attached to the bubbles, depending on the wettability of the fines. Figure 1.2 shows a simplified picture of the air-solids attachment process. The energy required to attach solids to air bubbles is expressed in terms of the free energy per unit area ΔG . The solids' attachment process involves three different interfaces: the water-solids interface, solids-air interface and air-water interface:

$$\Delta G = \gamma_{as} - \gamma_{sw} - \gamma_{wa}, \quad (1.2)$$

where ΔG is the free energy per unit area (J/m^2); γ_{sw} is the interfacial free energy of the solid-water interface (J/m^2); γ_{sa} is the interfacial free energy of the solids-air interface (J/m^2) and γ_{aw} is the interfacial free energy of the air-water interface (J/m^2). When the solids become hydrophobic, their affinity for water decreases, and the value of γ_{sw} increases. This increase leads to a decrease in the energy required for the attachment process, and hence the probability of solids attaching to the air bubbles increases. The solids report to the top layer of the PSV or flotation cell, leading to a decrease in the bitumen froth's quality. The solids wettability is not only critical for bitumen recovery but is also important for froth quality. As this

description of the extraction process indicates, the wettability of solids is one of the important factors governing the bitumen liberation.

1.3 Motivation and Objectives

The hot water extraction process (HWEP) is a physical-chemical separation process that uses the difference in the surface property of the valuable mineral (bitumen) and unwanted gangue minerals (fines and solids). The HWEP involves three-phases (water, solids, and bitumen) with many subprocesses and interactions which are not understood well. The processability (bitumen recovery) of oil sands ores correlates fairly well with oil sand grades and the fines contents of the solids component of the oil sands. High-grade ores usually have low fines and high bitumen content, and these ores have good processability. In contrast, low-grade ores have low bitumen content, and high fines content of the solids component of the ores, and exhibit poor processability (recovery). The poor processability of the ores has been attributed to the slime coating (attachment of fines to the bitumen surface) [13, 15]. The presence of fines not only reduces the recovery of bitumen but also affects the froth quality, leading to problems in the upstream processing of the bitumen. Some ores (ores that are stockpiled, suffering weathering or oxidization) are high in bitumen content and low in fines, but their processability is lower than that of even poor processing ores. The poor processability of some high-grade ores has been found to occur in industry as well as in laboratory processability tests (batch extraction unit tests); therefore, the poor processability of the oil sand ores cannot be credited to only the bitumen and fines content of the ores. Some other reasons might be responsible for the low bitumen recovery and poor froth quality of the bitumen froth. One of the goals of the present research was to study the wettability of the solids from different oil sand ores and to investigate if the wettability of the solids results in the poor recovery and poor froth quality of the ores. The second objective of the research was to find a relationship between the wettability of the solids extracted from oil sand and the processability of the ores. After establishing the effect of the wettability of solids on recovery and froth quality, attempts could be made to change the wettability of solids to improve the bitumen recovery as well as froth quality.

As the demand for the oil increases, more and more new leases are being explored and mined. Ores from different regions in an ore body could vary dramatically in terms of recovery. To respond to this variability, a simple and quick test which can mimic the hot water extraction process is needed. In the second part of this research, a simple procedure of jar tests was developed to assess the processability of ores both visually as well as quantitatively. The objectives of the present thesis are follows:

- To study the wettability of the solids extracted from different types of oil sands.
- To establish a relationship between the processability of ores and the wettability of solids from the ores.
- To develop a quick test to evaluate the processability of ores.

1.4 Thesis Organization

In Chapter 2, the experiments conducted to characterize oil sands and their processability, and the results of these experiments are discussed.

In Chapter 3, a detailed description of the solids isolation technique from oil sands is provided. Next, the techniques used to characterize solids are presented, and the results of the solids characterization experiments are presented and discussed.

In Chapter 4, the processability parameters determined in Chapter 2 are related to the wettability parameters determined in Chapter 3.

In Chapter 5, a quick visual jar test is developed to estimate the processability of the oil sand ores.

In Chapter 6, a summary of all chapters is presented, and recommendations for future work are suggested.

Chapter 2

Oil Sands Characterization

2.1 Introduction

In this chapter, the composition and processability of the different oil sands' ores used for the wettability study and jar tests are determined. The composition includes the bitumen, water, and solids content of oil sands. The fines content of the solids and the electrolyte content of the ores are also included in the oil sands composition determinations. The processability of the ores is determined using standard Denver flotation tests.

2.2 Source of Oil Sand Ores

Syncrude and Suncor generously provided the ores required for the research. Good processing and poor processing ores were procured from Syncrude, and oxidized ores were procured from Suncor. All the experiments were conducted in the Oil Sand Extraction labs, owned by the NSERC Oil Sands Research Chair in Oil Sands Engineering, located in the University of Alberta Chemical Engineering building.

Oil sands ores were crushed, chopped and homogenized in the Syncrude Research Center and packed in 500 g plastic bags. These bags were stored in a dark freezer at -26°C to inhibit any oxidation or weathering [18, 19]. The oil sand samples were thawed at room temperature in ambient air prior to each experiment.

2.3 Oil Sands Characterization

The characterization of each oil sands sample included determination of bitumen, water and solids content by using standard methods [2]. Since fines content of the solids fraction and the salt concentration of the water present in the in-situ oil sands have a huge impact on the oil sands' processability, fines and salt determinations were also included in characterizing the oil sands.

2.3.1 Bitumen, Water and Solids Content

The Soxhlet extraction-Dean Stark experiment is the most common method used to determine the bitumen, water and solids content of oil sands samples [2]. Schematic of the apparatus is shown in Figure 2.1.

One bag of oil sands weighing 500 g was randomly selected from the freezer and defrosted for 2 h before running the experiment. A thimble was filled with 40 g of oil sands and hung inside the extractor flask, which was filled with solvent (toluene). Toluene was refluxed in the extractor until the toluene dripping from the thimble became colour-less. With Dean Stark method, the sample was separated into bitumen, solids and water. Water was collected in the side arm of the Dean Stark trap, and was then poured into a weighed plastic bottle. The bottle was weighed again to determine the water content of the sample. The bitumen dissolved in the toluene was collected in the extractor flask. The bitumen toluene solution was transferred to a 250 mL measuring flask. If required, extra toluene was added to the flask to make the solution 250 mL in volume. The solution was drawn into a 5 mL pipette and spread on a pre-weighted filter paper. The filter paper was dried in a fume hood to evaporate the toluene, with the bitumen remaining on the filter paper. The dried filter paper was weighed to determine the bitumen content in 5 mL of the toluene bitumen solution, and the obtained value was multiplied by 50 to get the actual weight of the bitumen in the 40 g oil sands sample. The solids remaining in the thimble were weighed to determine the solids content. Thus, through the above procedure, the percentage of bitumen, water and solids in the oil sands sample was determined.

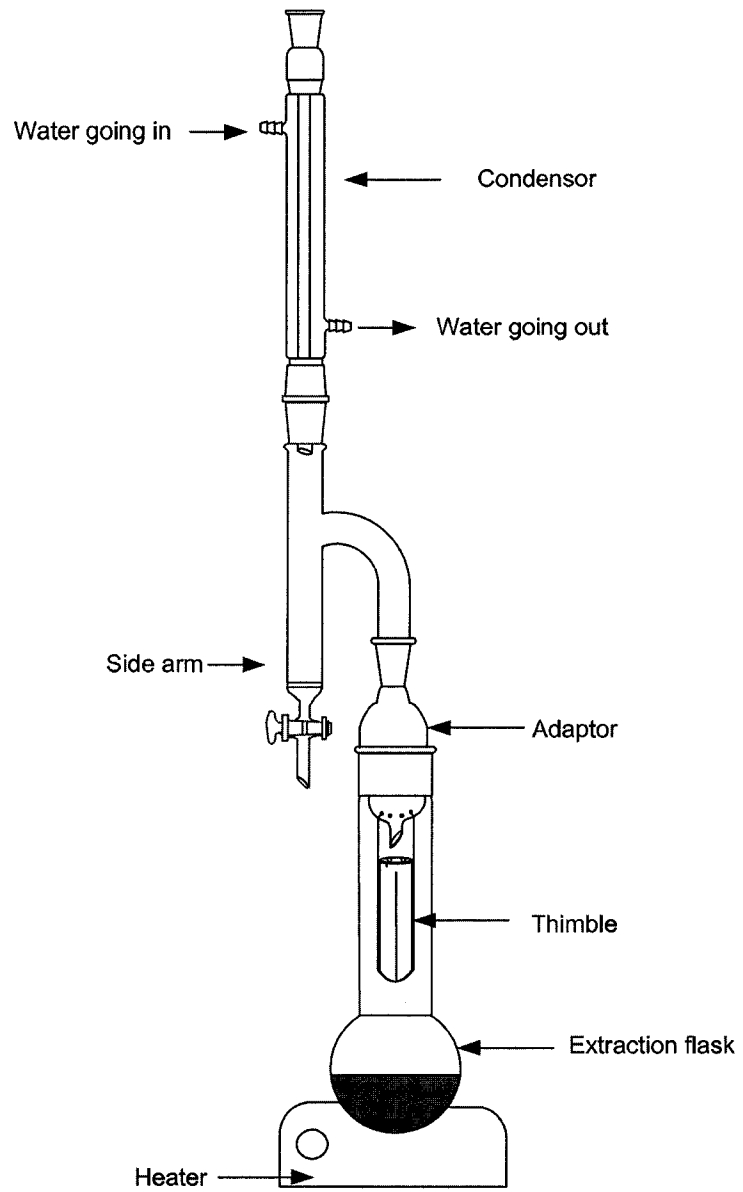


Figure 2.1: Schematic of Dean Stark apparatus

2.3.2 Fines Content

Fines are defined as solids smaller than 44 μm . Wet sieving [2] is the standard method for determining the weight percentage of fines in solids.

A 20 g oil sands sample was put into a 250 mL teflon centrifuge bottle, and 200 mL of toluene and isopropyl alcohol mixture (50:50 vol.) was added to dissolve the bitumen and water in the sample. The bottle was shaken in a standard shaker for 10 min and centrifuged at 2000g to avoid the loss of fines by using a MANDEL SORVALL^(R) Evolution^{RC} centrifuge. The supernatant was decanted, and fresh toluene was added. The shaking, centrifuging and decanting procedure was repeated until no more bitumen dissolved in the fresh toluene; i.e., the toluene remained colour-less even after shaking and centrifuging the sample. The extracted solids were then considered to be nearly bitumen-free. The solids and toluene mixture was wet-screened using a 45 μm sieve to separate the solids into two fractions, both of which were dried and weighed to determine the percentage of fines in the solids.

2.3.3 Electrolyte and pH Determination

A simplified hot water extraction [2] was conducted to determine the pH and electrolyte content of the oil sand samples.

A 50 g oil sands sample was mixed with 45 mL of boiling de-ionized water in a 250 mL beaker. The slurry was mixed with a spatula until a smooth paste was formed. The aqueous phase was decanted into a 30 mL centrifuge tube. The centrifuge tube was run at 20,000g centrifugal force, in a MANDEL SORVALL^(R) Evolution^{RC} centrifuge to remove the fines from the aqueous phase, and the oil film on the surface was removed by soaking with kimwipes. The clear aqueous phase was stored at 4°C and later sent to atomic absorption spectroscopy for cation determination. The pH of the clear aqueous solution was measured using a portable pH meter (OAKTON EUTECH Instruments, pH 110).

2.4 Processability Determination

The processability of the ores were assessed using a batch Denver flotation cell [17]. The procedure is known as either the Denver flotation test or the batch extraction test.

Table 2.1: Electrolyte content and pH of Aurora process water

Type of Ions	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	HCO ₃ ⁻	pH
Concentrations(mg/L)	48	19	14	503	647	8.2-8.4

The Denver flotation cell has recently been widely used to assess the processability of oil sands and to establish the effect of process aids and process variables [17, 22, 12]. A schematic representation of a Denver flotation system is shown in Figure 2.2. The flotation cell has a jacketed wall to allow a constant temperature during the test. Air was added through the impeller shaft to permit aeration of the slurry during the floatation of bitumen from the oil sands.

All recovery tests were conducted by using Aurora process water. The electrolyte content and pH of the process water are shown in Table 2.1.

Initially, hot water was circulated in the jacket at 35°C to provide a constant temperature during the test. A measured amount (950 mL) of process water was heated to 45°C in a 1 L beaker. A 300 g oil sands sample was added to the flotation cell, and subsequently, the warm process water was added. The impeller speed was adjusted to 1500 rpm, and the aeration rate was fixed to 150 mL/min. The impeller was lowered into the cell and switched on at the set rate for 5 minutes. After 5 minutes of conditioning time, the aeration was started, while collecting the froth using a spatula into four separate thimbles over 3, 2, 5, and 10 minute intervals, respectively. The thimbles were then placed and run in the Dean Stark apparatus (Section 2.3.1) to determine the water, bitumen, and solids content of the froth.

pH of the tailings water was also measured using a portable pH meter (OAKTON EUTECH Instruments, pH 110).

2.5 Results and Discussion

Generic names were given to the different ores that were tested. For each type of ore, at least four Dean Stark tests were conducted on the feed. The mean values of the bitumen, water, solids in the ores are reported in Table 2.2, with one standard deviation in the brackets. On the basis of the bitumen content, F11B, F11A, C, and SunOxy could be characterized as high-grade ores [10], and Posyn and D as low grade

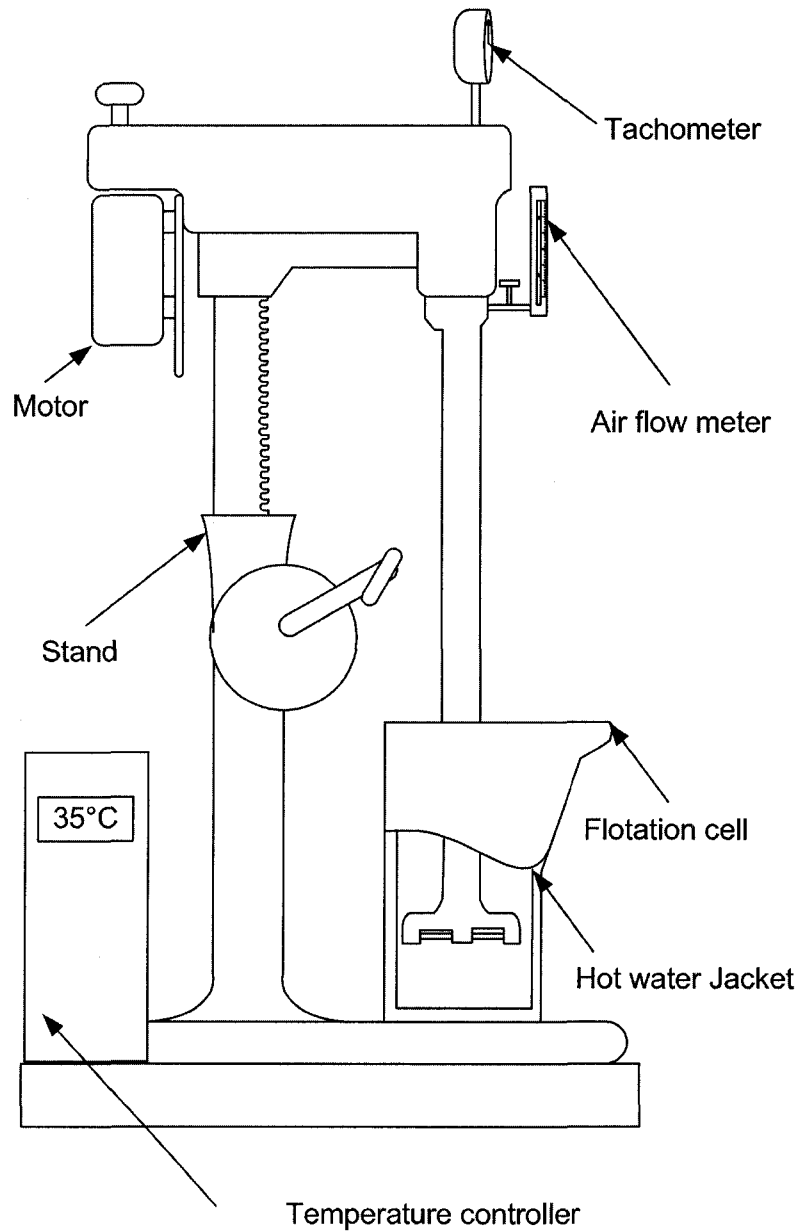


Figure 2.2: Schematic of Denver Cell (batch extraction unit)

Table 2.2: composition of oil sand ores [wt%]

Ores	%Bitumen	%Water	%Solids	%Fines
F11B	14.3(± 0.2)	3.9(± 0.1)	81.5(± 0.2)	6.0
F11A	14.6(± 0.3)	0.8(± 0.1)	84.2(± 0.3)	2.5
C	12.0(± 0.2)	1.0(± 0.1)	87.0(± 0.3)	5.5
SunOxy	12.1(± 0.3)	2.5(± 0.2)	84.1(± 0.1)	6.2
Posyn	5.5(± 0.1)	5.7(± 0.8)	88.9(± 0.2)	30.0
D	8.7(± 0.4)	3.6(± 0.1)	85.6(± 0.6)	20.3

Table 2.3: Electrolyte content (mg/kg of ore) and pH of the oil sand ores

Ores	Ca ²⁺ (mg/kg)	Mg ²⁺ (mg/kg)	Na ⁺ (mg/kg)	K ⁺ (mg/kg)	pH
F11B	1.6	0.2	80	10	7.1
F11A	1.9	0.3	110	2.2	7.2
C	75.2	10.4	29.4	3.4	5.6
SunOxy	8.2	4.2	47.3	0.8	5.7
Posyn	33.6	10.8	132	16.2	7.6
D	3.4	10.2	57.2	16.4	7.5

ores.

The electrolyte content of the ores is shown in Table 2.3. Since calcium and magnesium ions have a substantial impact on the processability of ores [15, 16], a comparison was made between the ores based on their electrolyte content. C and Posyn ores have relatively high electrolyte contents as compared to those of F11A, F11B, D, Sunoxy.

Flotation tests were conducted on the ores to determine their processabilities. Figure 2.3 shows the results of four duplicate runs of F11A ore. The cumulative recovery of the ore is plotted vs time. The error bars show one standard deviation on the cumulative recovery of F11A. The small value of the standard deviation indicated that the flotation tests were reproducible.

Assuming that the batch flotation process in the Denver flotation cell followed a first-order process, the flotation recovery (R) can be described by using Equation 2.1:

$$R = R_M(1 - e^{-kt}), \quad (2.1)$$

where $R_M(\%)$ stands for the ultimate flotation recovery; $k(\text{min}^{-1})$ stands for the flotation rate; and $t(\text{min})$ stands for the flotation time. Figure 2.4 was obtained by

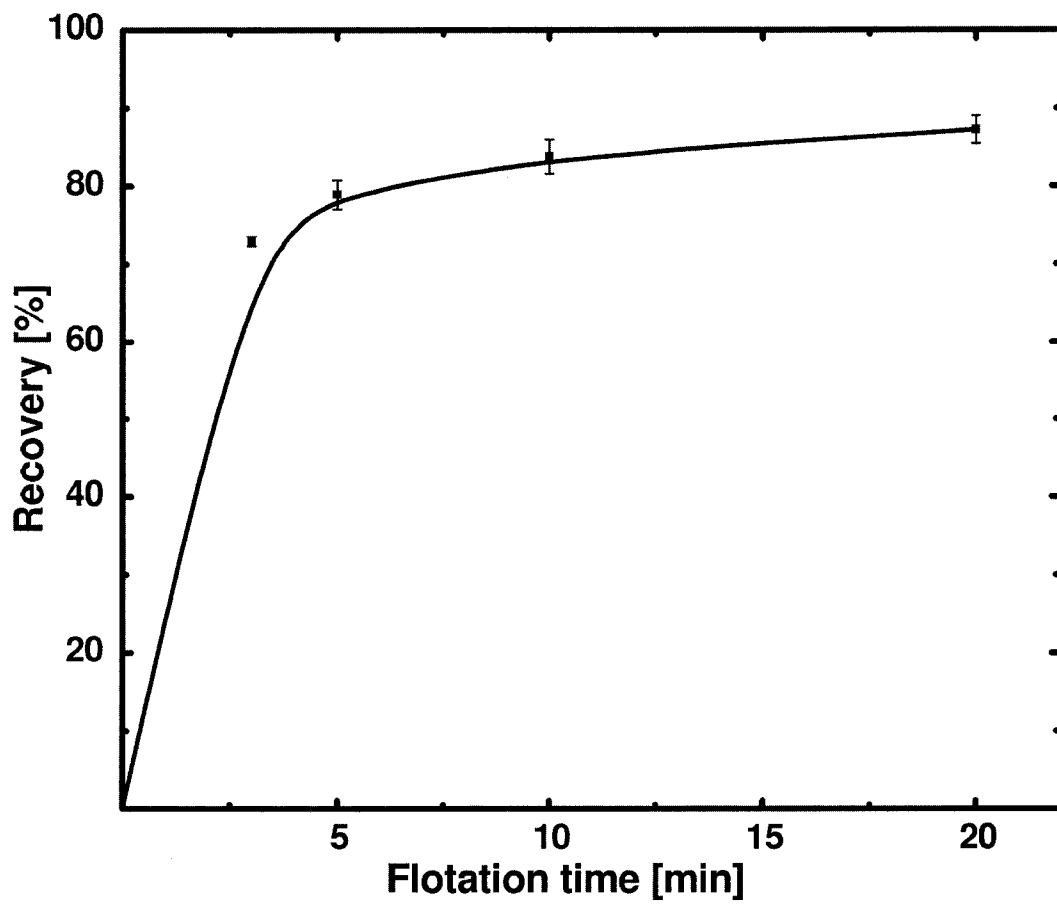


Figure 2.3: Flotation kinetics of good processing ore (F11A) with error bars

fitting the flotation experiment data with Equation 2.1, and $R_M(\%)$ and $k(\text{min}^{-1})$ were estimated for the different ores. The fitting was done by using non-linear fitting wizard of Origin 7.5 software. An exponential model with a boxlucas function was chosen for data fitting.

The estimated values are shown in the Table 2.4. The parameters $R_M(\%)$ and $k(\text{min}^{-1})$ are used to describe the processability of the ores. Ores F11A and F11B had relatively high ultimate recovery and flotation rate constants, whereas the other four ores had lower ultimate recovery and flotation rates. On the basis of the processability, ores F11A and F11B can be classified as good processing ores because they had high ultimate recovery as well as high initial flotation rates. The other four ores having relatively low ultimate bitumen recovery, were classified as poor processing ores.

The pH of the tailing water from different ores were measured and reported in Table 2.4. The pH of tailing water varied from 8.7-8.9, these pH were close to the pH of the Aurora process water.

Good processing ores are well known to have high bitumen content, low fines, and low concentration Ca^{2+} and Mg^{2+} in their ores [15, 16, 12, 22, 10]. For most of the ores, the percentage of fines in the solids from oil sands correlates well with the processability of ores [10, 15]. F11A and F11B had a lower percentage of fines as well as lower divalent cations in their ores and also showed good processability, so they were classified as good processing ores. Poor processing ores have low bitumen content, high fines and high Ca^{2+} and Mg^{2+} content in their ores [15, 16, 13]. The Posyn and D ores had comparatively lower bitumen content, higher fines and higher divalent cation concentration in their ores. The SunOxy and C ores had relatively high bitumen content and low fines, and still the recovery was low. This result may be attributed to the weathering or oxidization of the ores [10]. The pH of SunOxy and C ores was lower than 6 (pH of de-ionized water). This finding confirmed the presumption of oxidized ores. Sunoxy and C were categorized into a different category called oxidized ores, because of the acidic pH of the ores.

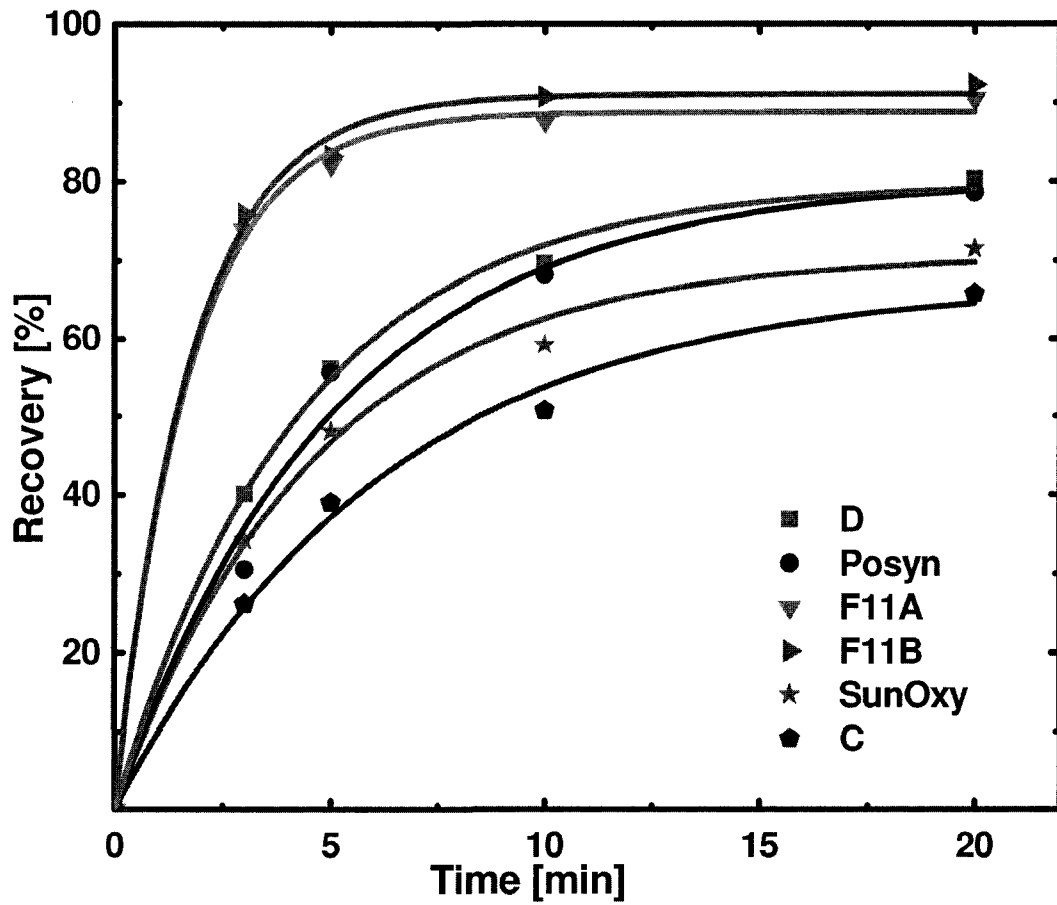


Figure 2.4: Flotation kinetics of different ores

Table 2.4: Flotation rate constant, ultimate recovery, froth quality and pH of tailings water of the ores

Oil Sands Ores	$k(\text{min}^{-1})$	$R_M(\%)$	Froth Quality	Tailing pH
F11A	0.57	88.8	2.5	8.7
F11B	0.57	91.0	3.4	8.8
C	0.16	67.2	1.2	8.5
SunOxy	0.22	70.8	0.4	8.6
Posyn	0.20	80.4	0.2	8.9
D	0.23	79.8	0.3	8.8

2.6 Summary

In this chapter, the composition of six different oil sands ores was determined. The fines content of the solids and the electrolyte content of the ores were determined. The ores were classified as good processing, poor processing and oxidized ores by using batch flotation tests. The poor processing ores had high fines and high electrolyte content in contrast to good processing ores which had low fines and electrolyte content. The Oxidized ores had typical low pH. In subsequent chapters, categories good processing poor processing and oxidized are used to identify the ores.

Chapter 3

Solids Wettability Characterization

3.1 Introduction

In this chapter, one ore from each of the categories of good processing, poor processing, and oxidized ores is selected. F11B is selected as a good processing ore, Posyn is selected as a poor processing ore, and SunOxy is selected as an oxidized ore. Solids are extracted from these ores, and their wettability is measured. The experimental techniques and the results are presented in this chapter.

3.2 Experimental Techniques

In order to determine the wettability of solids, they need to be isolated first. The standard Denver test was conducted to isolate solids. Solids were separated into a coarse fraction (-250 +106 μm) and a fine fraction (-45 μm). Film flotation and oil water partitioning tests were conducted for wettability characterization of the coarse solids from the different ores. The elemental composition of the coarse solids was determined by using X-ray photoelectron Spectroscopy (XPS). Initial contact angle measurement and the water drop penetration test were conducted for the fine fraction of solids from different ores.

3.2.1 Isolation of Solids from Oil Sands

Before any wettability test on solids can be conducted, the solids need to be isolated from the oil sands. The procedure adopted to extract solids is explained in this section.

Materials

Good processing ore (F11B), poor processing ore (Posyn), oxidized ore (SunOxy), and de-ionized water (pH 6.0-6.2, conductivity 10 M Ω cm) are used in the tests

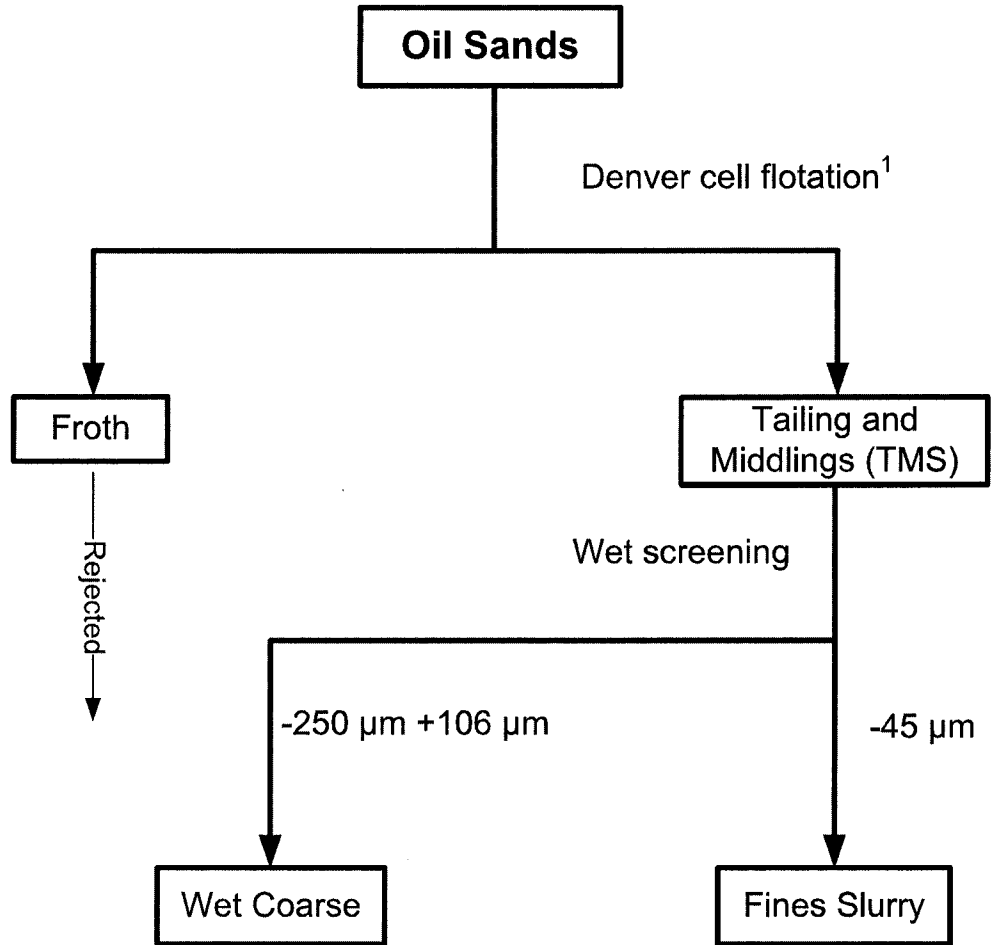
Apparatus

Denver flotation cell, sieves, spatula, shallow glass disc (10 mm diameter), and 2 L glass jars.

Procedure

A flow chart of solids extraction from oil sand ores is shown in Figure 3.1.

1. Set the rotor speed of a Denver flotation cell to 1500 rpm, the air flow rate to 150 mL/min, and the cell temperature to 35°C.
2. Add a 300 g oil sands sample and 950 mL de-ionized water pre-heated to 35°C, into the flotation cell.
3. Start the rotor at set speed for 5 minutes without aeration. This period is known as the conditioning period.
4. After 5 minutes of the conditioning period, start the air flow at the set rate.
5. Scoop the froth from the top of the cell and continue scooping for 1 h.
6. Switch off the rotation and aeration, and reject the collected froth.
7. Pour tailing and middling slurry (TMS), which is free of froth, from the flotation cell into a 2 L jar.
8. Wet sieve the TMS using sieves and de-ionized water to obtain the coarse (-250 +106 μ m) and fine (-45 μ m) solids fractions.
9. Keep the wet coarse fraction in a shallow glass disc and the fine fraction in a 2 L jar.



1. Flotation conditions: Temp: 35°C, flotation time: 1 h, speed: 1500 rpm, aeration: 150 mL/min, Water: De-ionized water

TMS: Tailings and Middlings Slurry

Figure 3.1: Solids isolation flow chart

3.2.2 Washing of Coarse Solids

The wet coarse solids obtained by using the procedure in Section 3.2.1 were washed by different solvents to establish the effect of solvent washings on the wettability of coarse solids. The coarse solids were dried and then washed with solvent to establish the drying effect on the wettability of the solids.

Materials

Analytical grade ethanol; analytical grade toluene; coarse fraction of solids (-250 +106 μm) of good processing, poor processing and oxidized ore; de-ionized water (pH 6.0-6.2, conductivity 10 M Ωcm); and kimwipes.

Apparatus

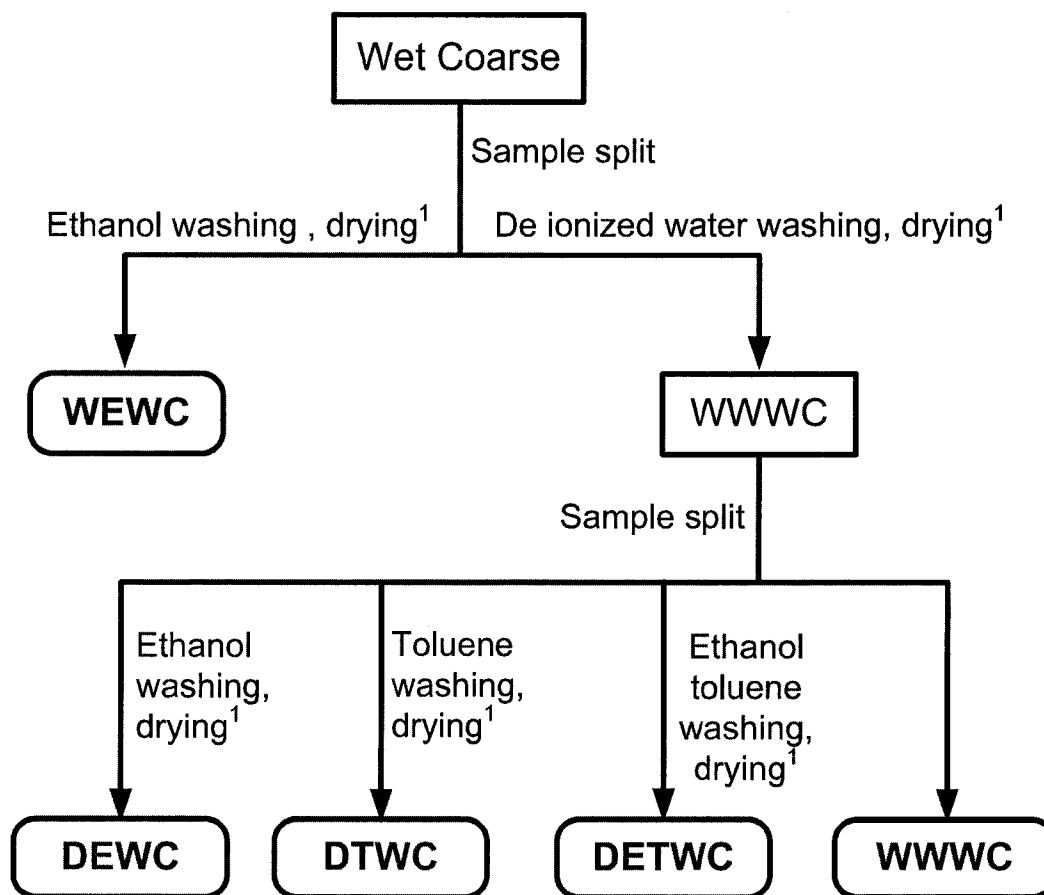
Shallow glass disc (10 mm diameter), spatula, 100 mL air tight jars, standard shaker.

Procedure

A flow chart of the solvent washing technique is shown in Figure 3.2.

1. Homogenize the coarse solids using the spatula, and spread them on a glass disc.
2. Divide the solids into four sectors by making two diagonal grooves with a spatula on the spread sample, and mix two opposite sectors to divide the coarse solids into two parts.
3. Transfer the first part of the wet coarse solids into a 100 mL jar, add ethanol, and shake the jar in a standard shaker for 10 minutes.
4. If the supernatant is not colourless, then discard the coloured ethanol, add extra ethanol, and shake the jar for 10 minutes; otherwise, go to next step.
5. If the supernatant is colourless, then transfer the solids onto a glass disc and dry them in a vacuum desiccator at room temperature; name the dried solids Wet Ethanol Washed Coarse (WEWC).

6. Transfer the second part of the wet coarse solids into a 100 mL jar, add de-ionized water to the wet coarse, and shake the jar in a standard shaker for 10 minutes.
7. Decant the extra water, transfer the solids onto a glass disc, and dry them in a vacuum desiccator at room temperature, name the dried solids there as Wet Water Washed Coarse (WWWC).
 - Homogenize the dried WWWC solids by a spatula, and spread them on a glass disc.
 - Divide the solids into four sectors by making two diagonal grooves on the spread sample by using a spatula, and mix two opposite sectors to split the coarse solids into two parts.
 - Divide the solids into 4 parts by repeating the previous steps.
 - Transfer the first part (Note: coarse solids are dry) into a 100 mL jar, add ethanol, and shake the jar in a standard shaker for 10 minutes.
 - If the supernatant is not colourless, throw-out the coloured supernatant ethanol, add extra ethanol, and shake the jar in standard shaker for 10 minutes; otherwise go to next step.
 - If the supernatant is colourless, then transfer the solids onto a glass disc, and place them in a vacuum desiccator for drying. Name the solids as Dry Ethanol Washed Coarse (DEWC).
 - Wash the second part (Note: Coarse solids are dry) with toluene using the same technique as that used with ethanol and name the solids Dry Toluene Washed Coarse (DTWC).
 - Wash the third part with both ethanol and toluene and name these solids Dry Ethanol Toluene Washed Coarse (DETWC).
 - Keep the fourth part as it is (WWWC).



WEWC: Wet Ethanol Washed Coarse solids

WWWC: Wet Water Washed Coarse solids

DEWC: Dry Ethanol Washed Coarse solids

DTWC: Dry Toluene Washed Coarse solids

DETC: Dry Ethanol Toluene Washed Coarse solids

1. Drying in dessicator under vacuum at room temperature

Figure 3.2: Flow chart of coarse solids washing

3.2.3 Film Flotation

A film flotation technique was used for the wettability characterization of coarse solids from different oil sands (see Figure 3.3). Film flotation experiments were conducted on all types of dried coarse particles. A small amount of particles were sprinkled over the surface of different methanol-water solutions. The sinking fractions were then collected and weighed to determine the amount of particles floating. The results were plotted as the cumulative percent of the floating vs the surface tension of probing liquids.

Materials

WWWC; WEWC; DEWC; DTWC; DTEWC from good processing, poor processing and oxidized ores; analytical grade methanol; and de-ionized water (pH 6.0-6.2, conductivity 10 MΩcm).

Apparatus

Film flotation apparatus (Figure 3.4), forcep, 50 cm diameter by 15 cm height aluminium disc, steel weighing disc, 1 L air tight jars, electronic balance (accuracy .0001 g), and KRÜSS Tensiometer K12.

Procedure

The step-by-step procedure of the film flotation experiment are shown in Figure 3.5.

1. Prepare 11 different methanol-water solutions by varying the water percentage from 0% to 100% (% vol.) at intervals of 10%. Keep the solutions in different air-tight jars.
2. Measure the surface tension of each solution by using KRÜSS Processor Tensiometer K12 at room temperature (22°C).
3. Weigh an aluminium pan, and place it below the ring of the film flotation apparatus.
4. Fill the apparatus with a methanol solution until the film of solution touches the lower edge of the ring.

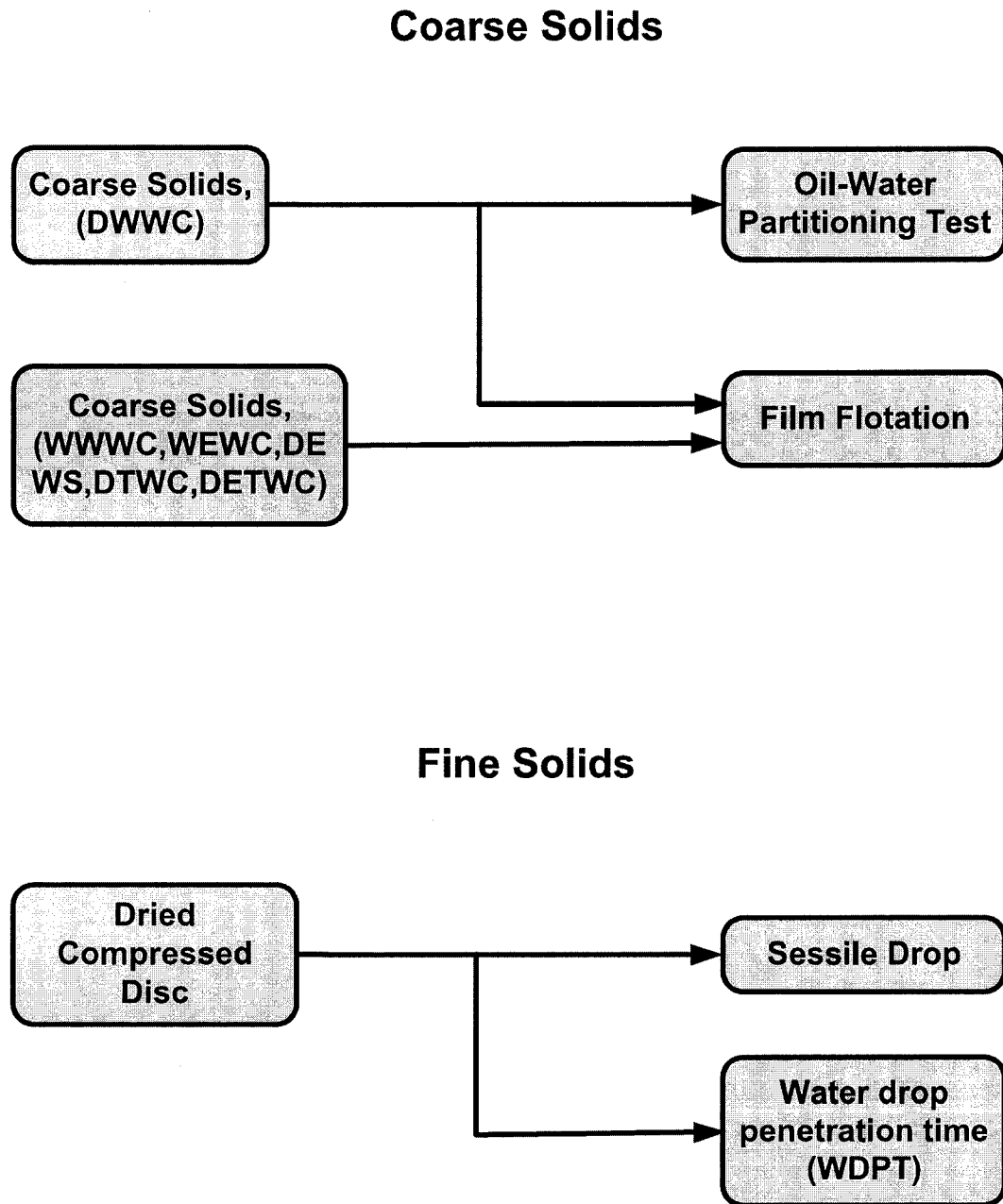
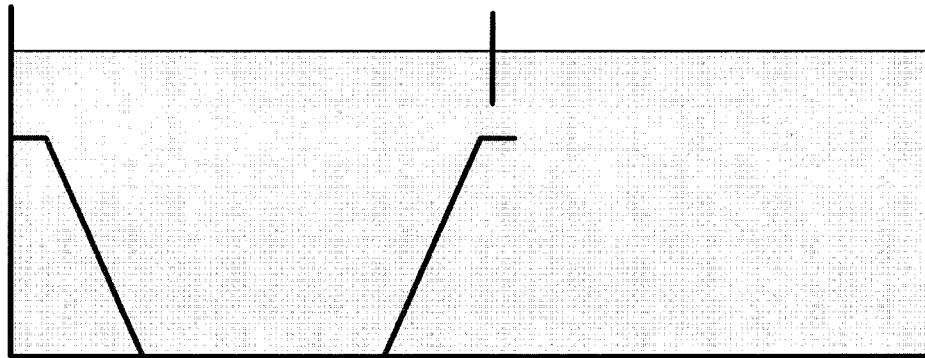


Figure 3.3: Different techniques used to study wettability of solids



Schematic showing the level of water-methanol solution in film flotation apparatus with respect to the aluminum pan

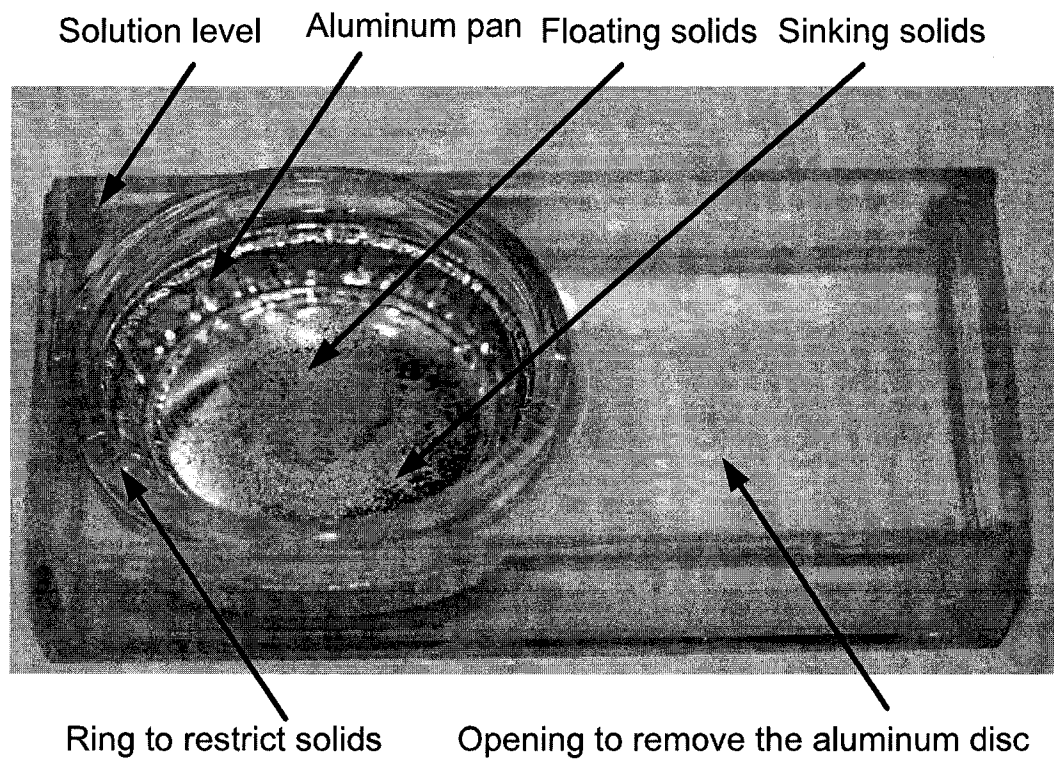


Figure 3.4: Film flotation apparatus

5. Place a weighing pan on the balance, and tare the balance.
6. Put approximately 0.05 g of solids onto the weighing pan.
7. Sprinkle the solids by placing the weighing pan from approximately 2 cm above the water level.
8. Reweigh the weighing pan to measure the weight of the solids being sprinkled onto the water film. This is done to account for particles that stick to the pan.
9. Remove the aluminum pan from the apparatus by forceps. The solids sunk are collected on this pan.
10. Dry the pan in a vacuum oven for 2 h, and then place it into a desiccator for 1 h to cool the pan.
11. Weigh the pan, and then place it again in the desiccator for 1 h. Reweigh the pan, if the weight of the pan is same as before then it confirms that the solids are completely free of solution.
12. Subtract the weight of the aluminum pan from the empty weight of the pan to determine the weight of the solids sunk.
13. Subtract the total weight of the solids sprinkled from the weight of sunk particles to determine the weight of the solids floating.
14. Repeat steps 3 to 13 for each of the remaining solutions.
15. Plot the percentage of the particles floating vs the surface tension of the probing liquid.

3.2.4 Oil Water Partitioning Test

Oil water partitioning tests were conducted to determine the fraction of the solids that were wet by water (hydrophilic). The WWWC solids from different ores are the most likely to be present in the hot water extraction process. This likelihood motivated the use of WWWC for the oil water partitioning tests.

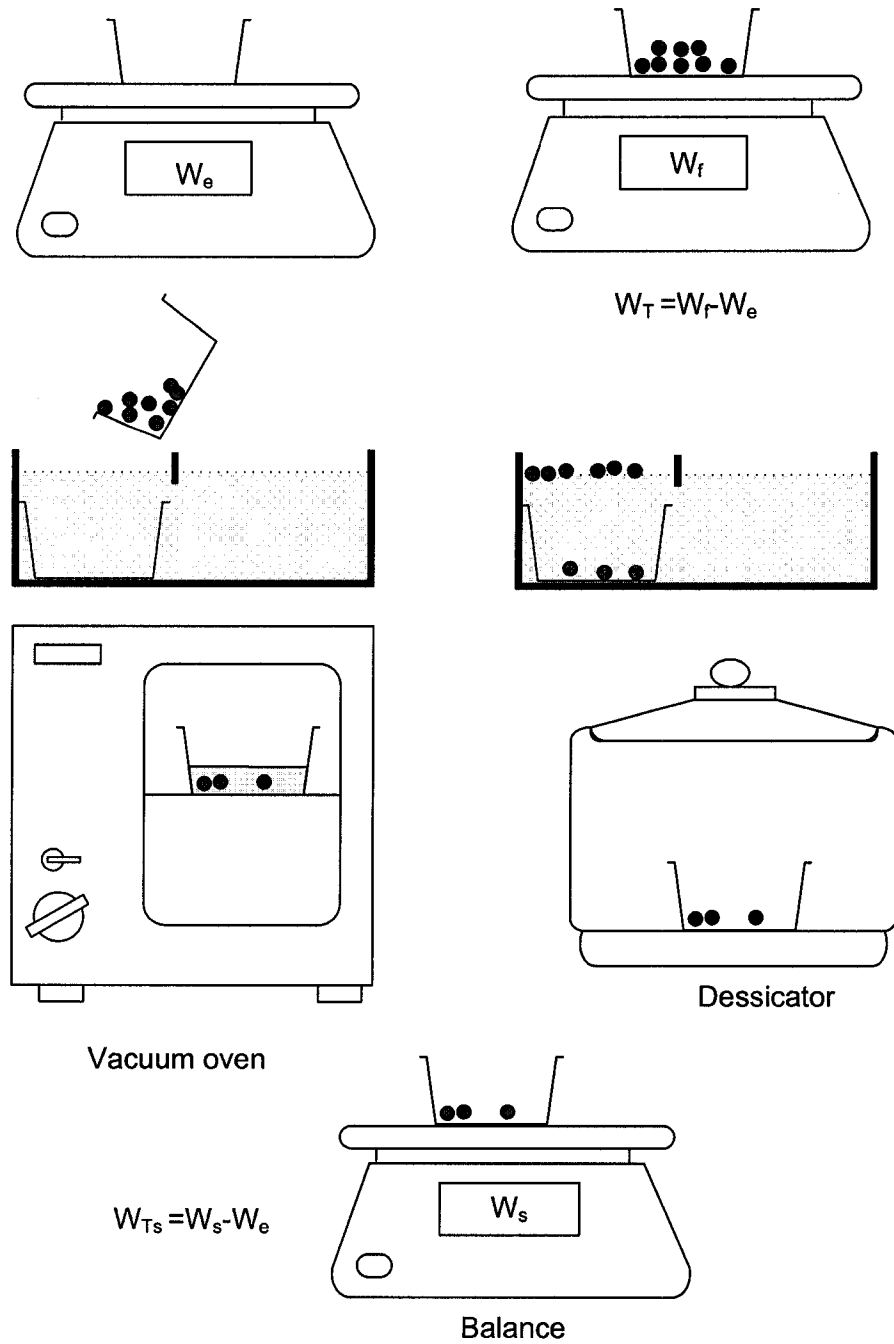


Figure 3.5: Film flotation method

Materials

Dried coarse solids from good processing, poor processing and oxidized ores after water washed while they were wet (WWWC); heavy mineral oil (viscosity at 40 °C is 34.5 centistokes and specific gravity 25 °C is 0.845); and de-ionized water (pH 6.0-6.2, conductivity 10 MΩcm).

Apparatus

Standard shaker and 25 mL glass bottles.

Procedure

1. Take a weighed amount (approximately 2 g) of dried WWWC solids in a 25 mL glass bottle.
2. Add 10 mL de-ionized water, and shake the jar to completely soak the solids with water.
3. Add 10 mL heavy mineral oil, shake the jar in a standard shaker for 10 minutes, and leave the sample undisturbed for 5 minutes.
4. Overflow the oil and oil wet solids by adding de-ionized water in aqueous phase to raise the oil/water interface ; if the overflowing oil is free of solids, then go to step 6; otherwise, go to the next step.
5. If the overflowing oil contains solids, then remove 15 mL clear water from the bottle, and go to step 3.
6. Dry the solids remaining in the bottle overnight in an oven at 160 °C to determine the weight of the remaining solids.
7. Determine the percent of the total solids that remain in the water phase.

3.2.5 X-ray Photo-electron Spectroscopy(XPS)

X-ray photo-electron spectroscopy is an excellent tool to determine elements present in the first 7 nm of the surface layer. XPS gives the elemental composition at the surface of the material under study. About 1 g of WWWC solids from different ores

were sent to the Alberta Centre for Surface Engineering and Science (ACSES) for XPS analysis.

3.2.6 Isolation of Fine Solids from Oil Sands

The isolation of solids was discussed in Section 3.2.1. Denver flotation was carried out to extract solids. The solids were sieved to split the solids into coarse and fine fractions. A fine slurry was obtained by using the procedure explained in Section 3.2.1. The method for obtaining the dry fine solids that were then used for the wettability characterization of fines is described in this section.

Materials

Fines slurry from good processing, poor processing and oxidized ores.

Apparatus

Centrifuge, 250 mL centrifuge bottle, shallow glass dish (10 mm diameter), vacuum oven, sieve, agate mortar and pestle, spatula, and 25 mL air-tight jars.

3.3 Procedure

A flow chart of the fines isolation technique is shown in Figure 3.6.

1. Decant the fine slurry into four centrifuge bottles, and balance the bottles.
2. Place the balanced bottles in the centrifuge, and run at 20,000g force for 20 minutes.
3. Remove the centrifuge bottles from the centrifuge, and decant the supernatant (almost free of fines).
4. Take out the fines' paste from the centrifuge bottles by using a spatula, and spread the paste on a glass dish.
5. Dry the paste in a vacuum oven until a constant weight is achieved.
6. Gently grind the fines by using an agate mortar and pestle, and then sieve the fines by using a $-45\mu\text{m}$ sieve.

7. Store the dried fines in an air-tight jars.

This procedure was applied to the good processing, poor processing and oxidized ores to isolate the fines from these ores.

3.3.1 Contact Angle Measurements

Fine solids from different ores were obtained using the techniques described in Section 3.2.6. The wettability characterization of fines was conducted using the techniques shown in Figure 3.3. Film Flotation for fines was not possible due to the difficulty of making a monolayer of fines by sprinkling [7]. Therefore, the WDPT test and initial contact angle measurements were conducted. Both techniques require a sample preparation (a compressed disc).

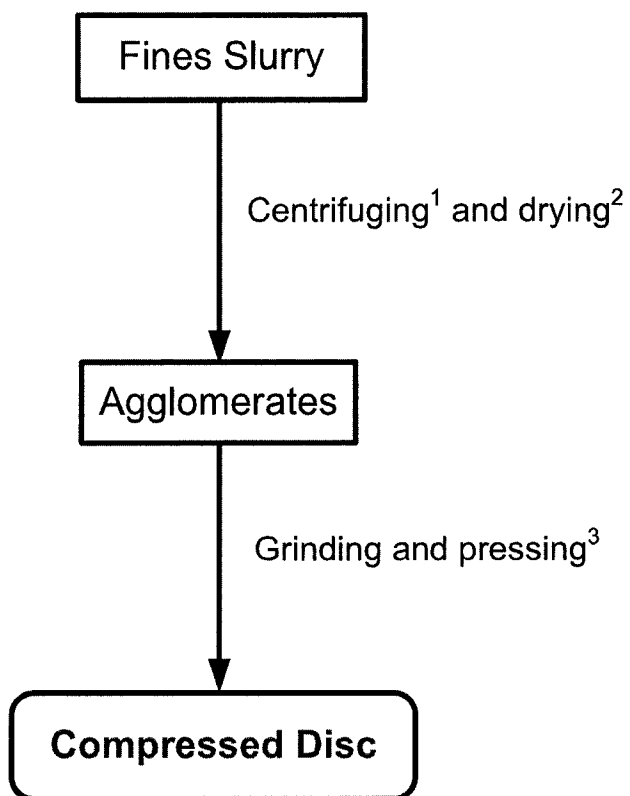
Sample Preparation

The experimental procedure for the compressed disc preparation is shown in Figure 3.7. The dried fines were compressed in a 1 inch die at a force of 6,000 lbf using an ENERPAC Press (Model No. JH-5) to a compressed disc of 5 mm thickness. The sample was kept under a compressive force of 6,000 lbf for two minutes. The compressed disc was then placed onto the glass slide, and the sample was immediately transferred to the contact angle measurement equipment.

Contact Angle Measurements

The contact angles were measured by a KRÜSS DSA (Drop Shape Analysis) 10 Mk2, which is equipped with a CCD camera. The system consists of a source of light with a diffuser, a microscope to which the CCD camera is connected, and a computer with DSA (Drop Shape Analysis) software designed for calculating the values of the contact angles. See Figure 3.8 for the simplified schematic of the instrumentation.

The DSA program calculates the contact angle of a drop of water placed on the substrate. Different methods can be employed to measure the three-phase contact angle. The Tangent Method was used, and the complete profile of a sessile drop was fitted to a general conic section equation. The derivative of the equation at the baseline gave the slope at the three-phase-contact point and thus the contact angle.



1. 20,000g centrifuging for 30 min

2. Drying in dessicator under vacuum at room temperature

3. Compressing at 6,000 lbf for 2 min

Figure 3.6: Fine solids isolation and preparation of compress disc

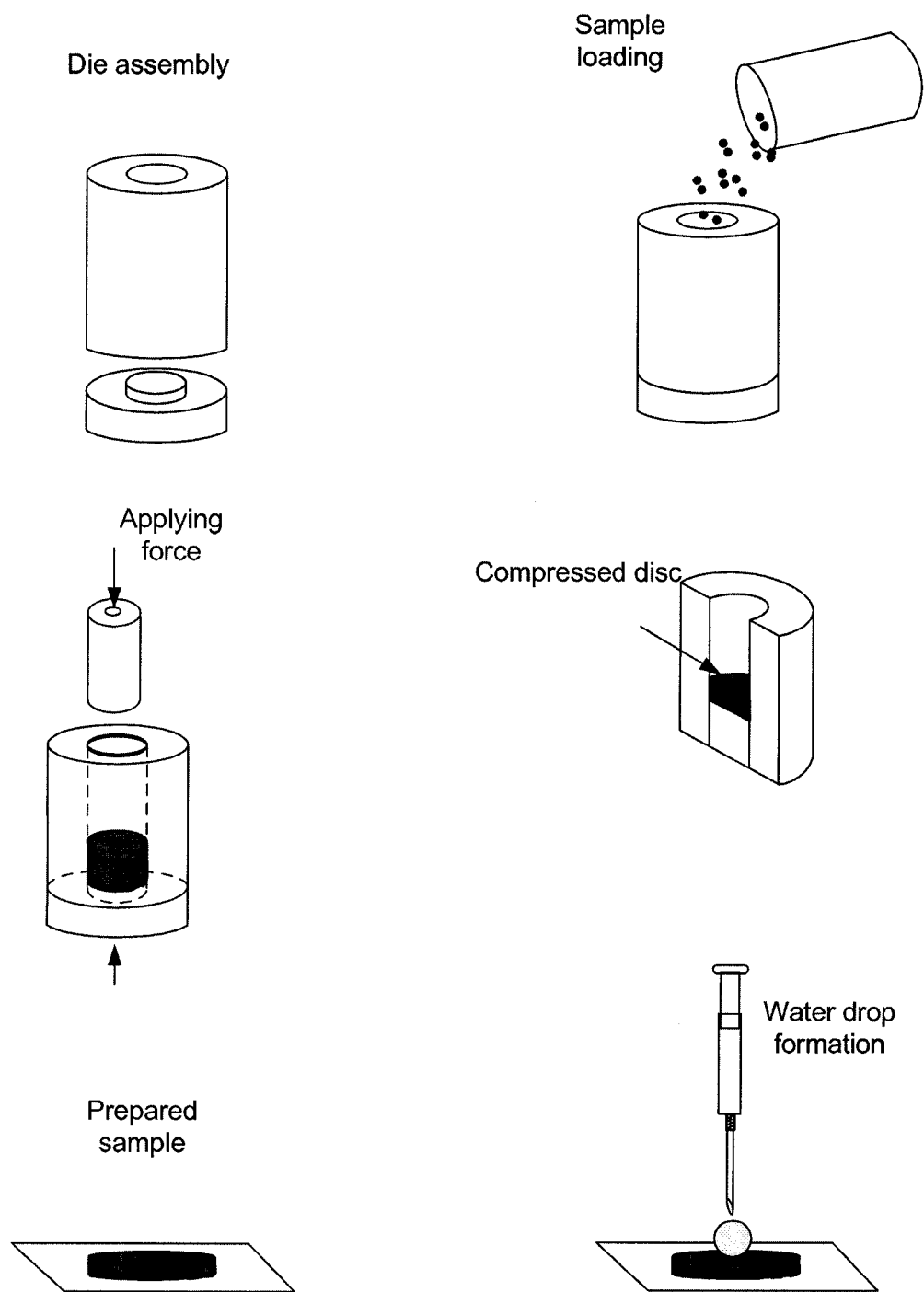


Figure 3.7: Procedure for compress disc sample preparation used in contact angle measurements and water drop penetration time measurements

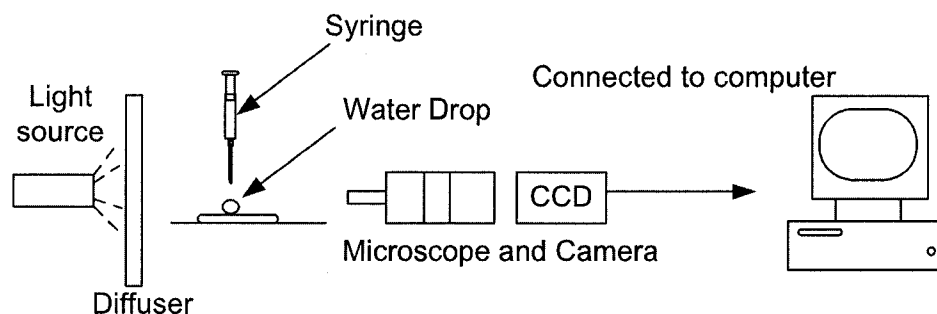


Figure 3.8: Schematic of experimental set-up for contact angle measurements

The sessile drop technique was used to determine the initial contact angle of the compressed fines obtained from different ores. A 10 μL de-ionized water (pH 6.0-6.2) drop was placed on the compressed fines in the air by a micro-syringe. The picture of water drop was taken by a CCD camera. The picture was processed to determine the three-phase contact angle. The contact angle was measured as soon as the drop was placed on the surface to avoid a change in the contact angle due to the absorption of water by the sample. The angle measured as such was called the initial contact angle.

3.3.2 Water Drop Penetration Time Test (WDPT)

The water drop penetration time test is a technique used in soil science to evaluate water repellency of the soil [14, 1]. In this technique, the time taken by a water drop to penetrate the soil sample is measured. This test was conducted for the fines obtained from different ores.

Sample Preparation

Sample preparation was same as that for contact angle measurement. The dried fines were compressed in a 1 inch die at a force of 6,000 lbf using an ENERPAC Press (Model No. JH-5) to a compressed disc of 5 mm thickness. The sample was kept

under a compressive force of 6,000 lbf for two minutes. The compressed fines were used directly for water drop penetration time measurements.

Water Drop Penetration Time Measurement

The compressed disc was transferred to the contact angle measurement equipment. A 10 μL de-ionized water drop was placed on the surface of the compressed fines, and real-time video of the drop penetrating the sample was taken by a CCD camera and DSA software. Similarly, two more drops were placed, leaving 5 mm space between the drops to avoid the effect of other drops on the water drop penetration time. This procedure was repeated for all the samples, and at least 9 observations were made for each ore type. The stored videos were later analyzed to determine the water drop penetration time of the compressed fines.

3.4 Results and Discussion

The results and discussion of the different experiments conducted for the wettability characterization of coarse solids as well as fines are presented in this section.

3.4.1 Solids Isolation

Solids were isolated from oil sands using the standard Denver flotation test. The solids obtained after 1 h of flotation could be considered bitumen-free because the froth generated was negligible after 1 h of flotation. This procedure was repeated for the good processing, poor processing and oxidized ores to get the coarse fraction as well as the fines fraction of the ores.

3.4.2 Coarse Solids Washing Technique

The coarse solids obtained after the Denver flotation were dried and washed using different solvents. This procedure was conducted to establish the effect of solvent washing on wettability of solids. Ethanol and toluene were used as solvents to wash the coarse solids.

Ethanol was chosen as a solvent because it can dissolve water and is a good reagent that can remove surfactants from the surface of solids. Surfactants are present in the

oil sands and are released into the water when the flotation of ores is conducted in a flotation cell. Surfactants have a tendency to adsorb on the solid surfaces. The process may lead to a change in the surface property of solids.

Toluene was used as a solvent to wash the dried solids as it can remove the bitumen that may still remain on the surface of solids even after 1 h of flotation. The presence of bitumen can make the surface of solids hydrophobic.

The solvent washing procedure was conducted for the solids from the good processing, poor processing and oxidized ores. For every ore, WWWC, WEWC, DTWC, DEWC, DETWC solids were prepared. The wettability of the solids was measured using the film flotation technique. Oil-water partitioning tests were conducted for WWWC from the poor processing, good processing and oxidized ores. Figure 3.3 shows the techniques used to conduct wettability characterization of the coarse solids.

The results for the coarse and fine solids characterization are presented in the following section. Film flotation tests were conducted for all the coarse solids, and the effects of solvent washing on the wettability of solids were established. The difference in the wettability of solids from different oil sands was also established.

3.4.3 Film Flotation Results

The wetting behavior of coarse solids from different oil sands and the effect of solvent washing on solids wettability were investigated through film flotation experiments by varying the surface tension of the liquid between 72.5 mJ/m² of de-ionized water and 22.4 mJ/m² of pure methanol. The surface tension measurements were conducted at room temperature. Figure 3.9 shows the variation of the surface tension of the aqueous methanol solution. The measured value was compared with the values from CRC handbook. The measured surface tension was very close to the values from CRC handbook.

Depending on the wetting characteristics of the solids and the surface tension of the liquid solution used, the particles either remained at the liquid/vapor interface or immediately sank into the solution. Subsequently, the hydrophobic (floating) and hydrophilic (sinking) fractions were recovered, dried and weighed. Unless otherwise specified, all film flotation experiments in this research were carried out using -250 +106 μ m particles and aqueous methanol solutions as the wetting liquid at 22°C

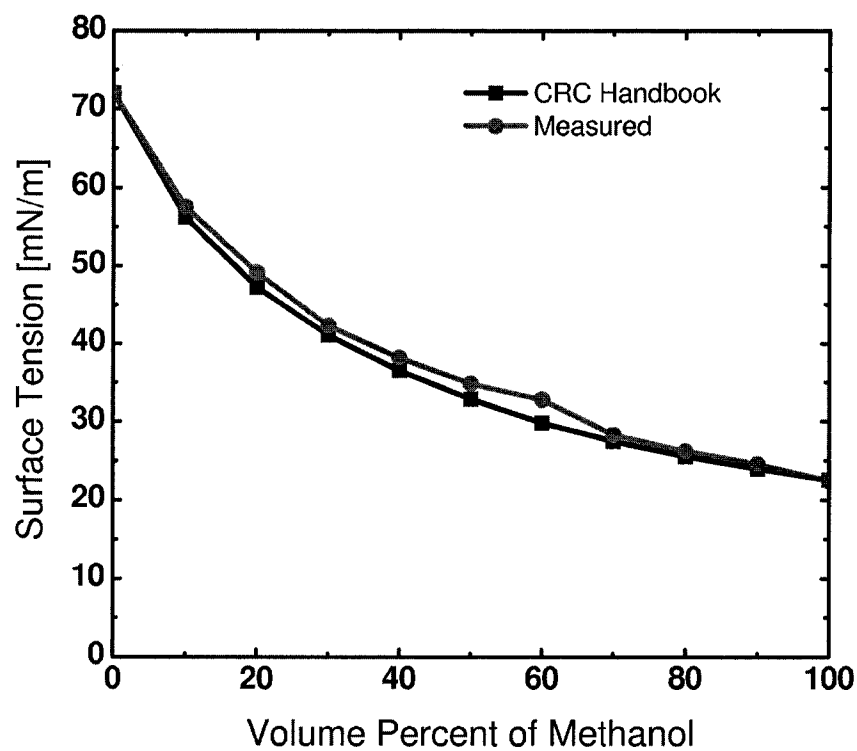


Figure 3.9: Surface tension of methanol-water solution as a function of the volume percent of methanol in liquid

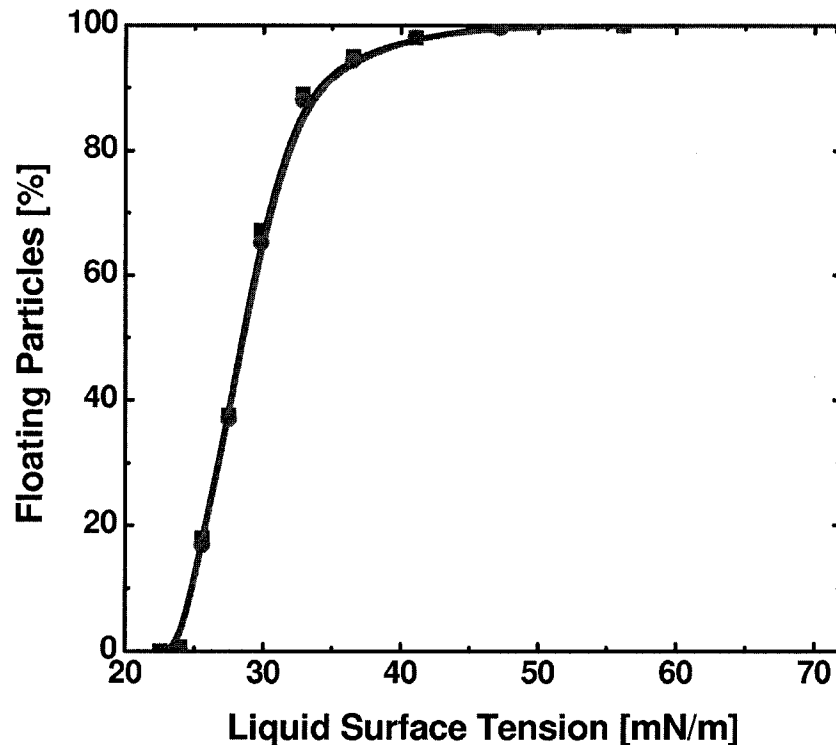


Figure 3.10: Film flotation partition curve of coarse solids from good processing ores: two sets of data from duplicate runs

room temperature. The percent of solids floating was calculated and plotted as a function of the surface tensions of probing liquids.

Two duplicate experiments were conducted on the dried “wet water washed coarse” solids to investigate the reproducibility of the film flotation test. Figure 3.10 shows the partition curves of the dried “wet water washed coarse” solids obtained from film flotation of two duplicate runs. The results in Figure 3.10 show that the film flotation experiment is reproducible, and can be performed accurately.

Because of the heterogeneity of solids from oil sands, the wetting behavior of coarse solids may vary from that of hydrophobic organic materials to that of hydrophilic inorganic matter. From the results given in Figure 3.10, the mean critical wetting surface tension of the coarse solids can be obtained.

The mean critical wetting surface tension of all particles, $\bar{\gamma}_c$, can be calculated from the cumulative partition curve shown in Figure 3.10. Equation 3.1 is used to determine the mean critical wetting surface tension of the particles [7, 5, 9, 8, 6]:

$$\bar{\gamma}_c = \sum (\gamma_L)_i f_i(\gamma_L), \quad (3.1)$$

where $(\gamma_L)_i$ is the surface tension of the probing liquid, and $f_i(\gamma_L)$ is the weight fraction of solids that sink at $(\gamma_L)_i$. The mean wetting surface tension $\bar{\gamma}_c$ is a parameter used as an index to characterize the wettability of coarse solids. The mean critical wetting surface tension of the coarse solids obtained from different oil sands was determined.

A shift in the partition curves, obtained from the film flotation experiments, towards the right indicates a decrease in the hydrophobicity of the solids. By studying the curves, a relative judgment about the hydrophobicity of the solids can be made [7, 5, 9]. The mean critical wetting surface tension (MCWST) of the solids can be determined to characterize the wettability behavior of solids. The solids having higher values of mean critical wetting surface tension represent hydrophilic solids as compared to the solids with a lower mean critical wetting surface tension [9, 8].

Film Flotation Response of Coarse Solids from Different Ores

Film flotation was conducted on the dried “wet water washed coarse solids” (WWWC) isolated from the good processing (F11B), poor processing (Posyn) and oxidized (SunOxy) ores. Refer to Section 3.2.1 and Section 3.2.2 for the detailed procedure for coarse solids isolation and the film flotation technique. Figure 3.11 shows the film flotation partitioning curves of the coarse solids. Moving from left to right in the figure, the hydrophobicity of the solids decreases. Figure 3.11 shows that the partition curve from coarse solids of good processing ores lies in the right-most part of the figure, whereas the curve for the oxidized ores lies in the left-most. The partition curve from the poor processing ores lie between the partition curves for good processing and oxidized ores from coarse solids. The right-most curve indicates that coarse solids from good processing ores are hydrophilic as compared to the coarse solids from poor processing and oxidized ores. The left-most curve in Figure 3.11 belongs to the oxidized ores and indicates that coarse solids from oxidized ores are the most hydrophobic among the three ore types.

Table 3.1 shows the mean critical wetting surface tensions of “wet water washed coarse solids” from different ores, calculated by using Equation 3.1 and Figure 3.11.

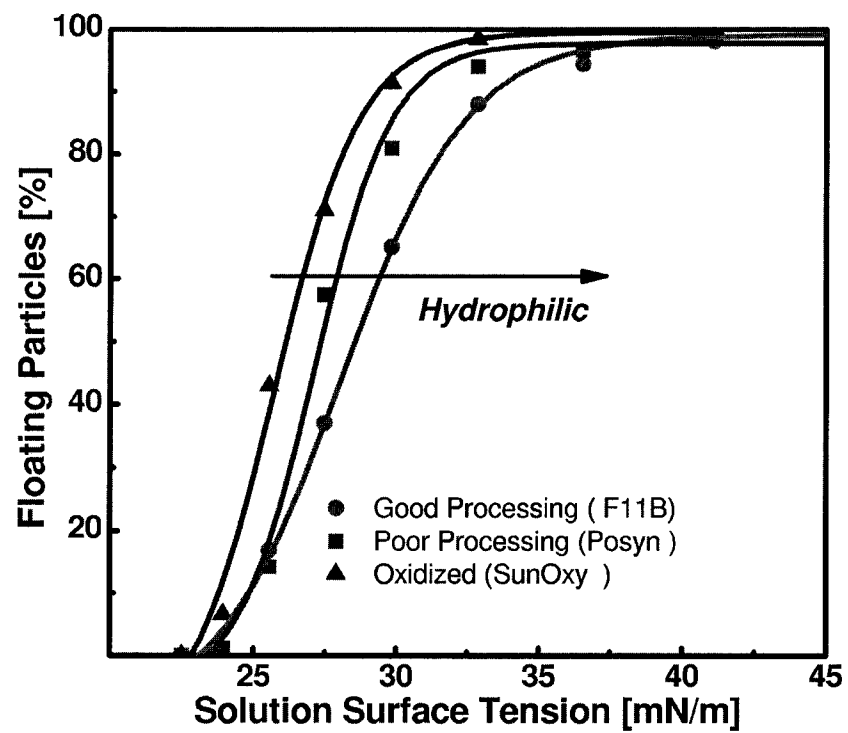


Figure 3.11: Partitioning curve for film flotation of dried “wet water washing coarse” solids from different ore

Table 3.1: Mean critical wetting surface tensions of “wet water washed coarse” solids from different types of ores

Oil Sands Ores	Mean Critical Wetting Surface Tension (mN/m)
Good Processing Ore	27.9
Poor Processing Ore	24.1
Oxidized Ore	23.4

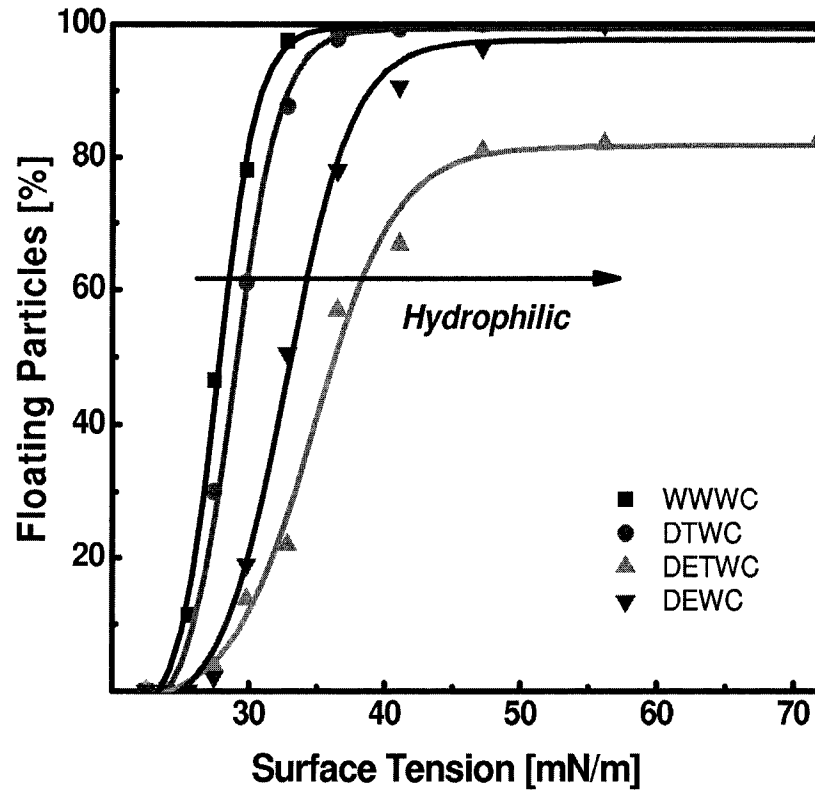
A higher value of mean critical wetting surface tension for the solids from the good processing ore indicates that the coarse solids were less hydrophobic in comparison to the solids from other ores. The coarse solids from the oxidized ores had the minimum value of the mean critical wetting surface tension, indicating that these coarse solids are the most hydrophobic.

Table 3.1 and Figure 3.11 suggest that the hydrophobicity of dried “wet water washed coarse” solids increased from the good processing and poor processing to oxidized ores. One of the reasons might be that the percentage of the bitumen removed after 1 h flotation was less for the oxidized ores and poor processing ores than that for the good processing ores. Thus, more bitumen remained on the surface of the solids in the case of the oxidized and poor processing ores than in the case of the good processing ores. To confirm this assumption, surface elemental compositions of the solids were determined using x-ray photoelectron spectroscopy (XPS). The results are presented in Section 3.4.5. The presence of bitumen on solids can make the solids hydrophobic.

Film Flotation Response of Solvent Washed Coarse Solids

The dried “wet water washed coarse” solids were washed with different solvents to study the effect of solvent washing on the wettability of coarse solids. The washing procedure is explained in Section 3.2.2. If the solids were washed with ethanol, they were called DEWC, and if washed with toluene, they were named DTWC. Solids were also washed with both ethanol and toluene and named DETWC.

Figures 3.12 and 3.13 show the effect of solvent washing on the wettability of coarse solids from good processing and poor processing ores, respectively. The solids became less hydrophobic when washed with toluene, and even less hydrophobic when washed with ethanol. When the coarse solids were washed with ethanol and toluene,



WWWC: Wet Water Washed Coarse

DTWC: Dry Toluene Washed Coarse

DTEWC: Dry Ethanol Toluene Washed Coarse

WWWC: Dry Ethanol Washed Coarse

Figure 3.12: Effect of solvent washing on wettability of coarse solids from good processing (F11B) ore

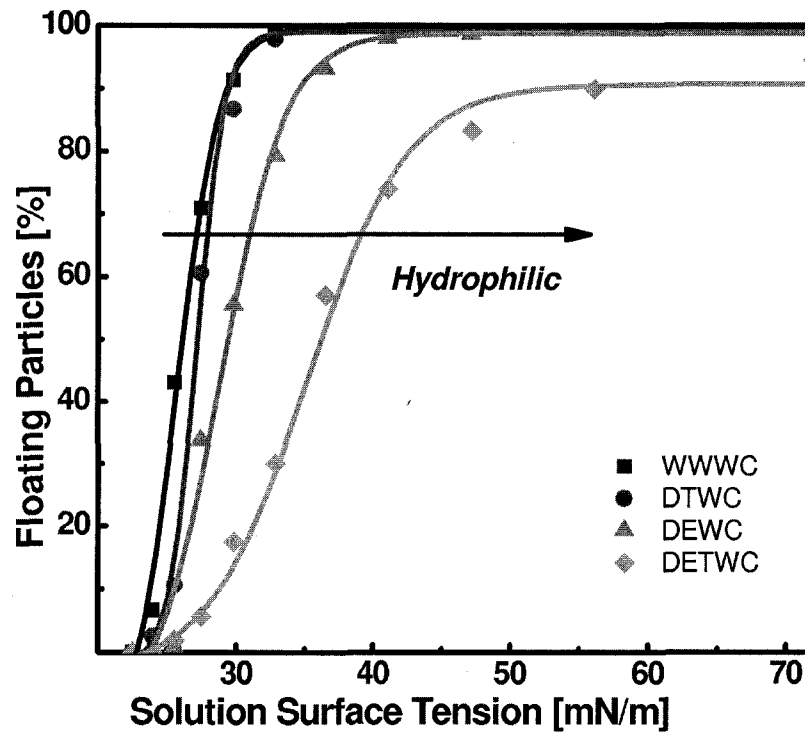
they became the least hydrophobic as compared to the solids washed with toluene or ethanol alone. A similar conclusion could be made from the mean critical wetting surface tension values shown in Table 3.2 for the different coarse solids.

The results in Figure 3.12, Figure 3.13 and Table 3.2 suggest that the dried “dry toluene washed coarse” (DTWC) solids were less hydrophobic than the dried “wet water washed coarse solids” (WWWC). The reason might be that some bitumen from the surface of the solids was removed during the washing with toluene. This bitumen could not be removed from solid surface even after 1 h flotation. The presence of bitumen on the surface of solids makes coarse solids hydrophobic as bitumen is inherently hydrophobic in nature. Thus, once the bitumen was removed from the surfaces by toluene washing the solids became less hydrophobic.

The results in Figure 3.12, Figure 3.13 and Table 3.2 also show that ethanol washing makes solids more hydrophilic than water washing and toluene washing. It appears that ethanol washing might have removed the surfactants that were released from the oil sands during the hot water extraction process.

Furthermore, the results in Figure 3.12, Figure 3.13 and Table 3.2 show that washing solids with ethanol and toluene makes the surface of the solids the least hydrophobic in comparison to toluene washing or ethanol washing alone. The reason might be that the toluene removed the bitumen from the solids, and the ethanol removed the surfactants. In this case the compounds most probably responsible for the hydrophobic nature of solids were removed by washing the solids with both ethanol and toluene; hence the solids became the least hydrophobic.

Solvent washing had a similar effect for solids from good processing, poor processing and oxidized ores. The results in Figure 3.12 and Figure 3.13 demonstrate that washing with solvents changes the wettability of coarse solids. Table 3.2 shows the mean critical wetting surface tension of different solids obtained after washing with different solvents. It can be inferred from the mean critical surface tension values that regardless of the ores from which the solids were isolated, the solids became less hydrophobic when washed with solvents like ethanol and toluene. These results establish that solvent washing has the capability to change the surface properties of solids.



WWWC: Wet Water Washed Coarse
DTWC: Dry Toluene Washed Coarse
DEWC: Dry Ethanol Toluene Washed Coarse
DETC: Dry Ethanol Washed Coarse

Figure 3.13: Effect of solvent washing on wettability of coarse solids from poor processing (Posyn) ore

Table 3.2: Effect of solids washing with different solvents on mean critical wetting surface tension obtained from film flotation test data

Oil Sands Ores	Water	Ethanol	Toluene	Ethanol Toluene
Good Processing Ore (F11B)	27.9	40.3	28.3	41.1
Poor Processing Ore (Posyn)	24.1	28.9	25.9	35.7
Oxidized Ore (SunOxy)	23.4	25.1	26.0	36.9

Table 3.3: Effect of dried solids washing and wet solids washing with ethanol on mean critical wetting surface tension obtained from film flotation results

Oil Sands Ores	Dried Ethanol Washed (mN/m)	Wet Ethanol Washed (mN/m)
Good Processing Ore (F11B)	40.3	60.6
Poor Processing Ore (Posyn)	28.9	54.4
Oxidized Ore (SunOxy)	25.1	52.3

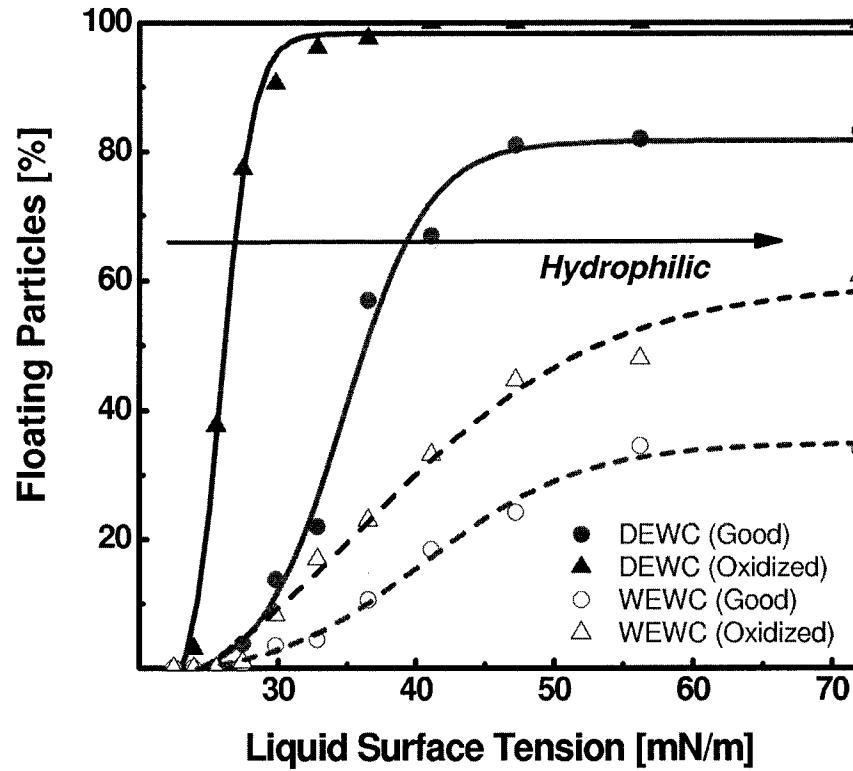
Film Flotation Response of Dried and Wet Washed Coarse Solids

The coarse solids obtained after oil sands flotation were washed when they were still wet and washed after drying the solids to study the effect of drying on the wettability of coarse solids. Ethanol was used because it can wash wet solids as it is miscible with water. If toluene were used instead, an emulsion could have formed when the solids were wet washed. Coarse solids were named “wet ethanol washed coarse” (WEWC) when wet solids were washed with ethanol. The coarse solids were named “dried ethanol washed coarse” (DEWC) when washed with ethanol after solids were first dried. A film flotation experiment was conducted on the wet washed solids and dried washed solids to establish the effect of drying.

Figure 3.14 and Table 3.3 show that the “wet ethanol washed coarse” solids were less hydrophobic than the “dry ethanol washed coarse” solids. If the solids were washed with ethanol when they were still wet, the surfactants present in the water medium of the flotation experiments did not get attached to the surface of coarse solids and were removed when washed with ethanol. When the coarse solids were dried and then washed with ethanol, they were more hydrophobic than the wet washed solids. It is possible that the surfactants in water got attached to the surface of the solids during drying, hence making them hydrophobic. Even washing with ethanol after drying could not remove all the surfactants hence, the surface were more hydrophobic.

3.4.4 Partitioning Test Results

The oil-water partitioning test is also known as a two-phase separation test. A measured amount of solids is shaken with water and mineral oil. The solids remaining in the water phase were called hydrophilic solids, the solids remaining in the oil phase



WEWC: Wet Ethanol Toluene Washed Coarse

DTEWC: Dry Ethanol Toluene Washed Coarse

Figure 3.14: Effect of drying on partitioning of solids during film flotation of ethanol washed coarse solids

were called hydrophobic solids. Using this method, solids could be easily separated into hydrophobic and hydrophilic fractions. Since the theory behind this experiment needs to be developed, not all types of solids were characterized using this technique. Only wet water washed coarse solids were tested to establish if this test could distinguish the solids from different ores.

The percentage of solids in the water phase can be used as an index to estimate the wettability of solids.

The partitioning test was conducted on dried wet water washed coarse solids obtained from the good processing, poor processing, and oxidized ores. Figure 3.15 shows the photograph of the solids in the water and oil phases. The photograph shows that compared with the solids from poor and good processing ores more solids from the oxidized ores are in the oil phase. The good processing ore had the lowest percent of solids in the oil phase. The quantitative values of the solids in the water phase for different ores is shown in Figure 3.16. Clearly, the percentage of hydrophilic solids in good processing ore is more than that in poor processing and oxidized ores. The oxidized ores have the lowest percentage of hydrophilic coarse solids.

The results of the oil-water partitioning tests suggest that coarse solids from good processing ores have a greater fraction of hydrophilic coarse solids than poor processing and oxidized ores.

3.4.5 XPS Results of Wet Water Washed Coarse Solids

The surface elemental composition of the wet water washed coarse solids was determined by x-ray photo-electron spectroscopy to support the wettability behavior of coarse solids as determined by film flotation and oil water partitioning tests. The results of the XPS analysis are presented in Table 3.4, which provides a brief summary of the mass concentration of selected elements in the surface layer of the wet water washed coarse solids. The poor processing ore and oxidized ores had a relatively higher percentage of carbon, indicating a higher percentage of organic carbon on the solids from these ores than from the good processing ores. The organic carbon on the surface of the solids may come from bitumen that could not be removed after flotation of the oil sands. The organic carbon on the surface of solids makes the surface hydrophobic, and a higher percentage of silicon and aluminum makes the surface

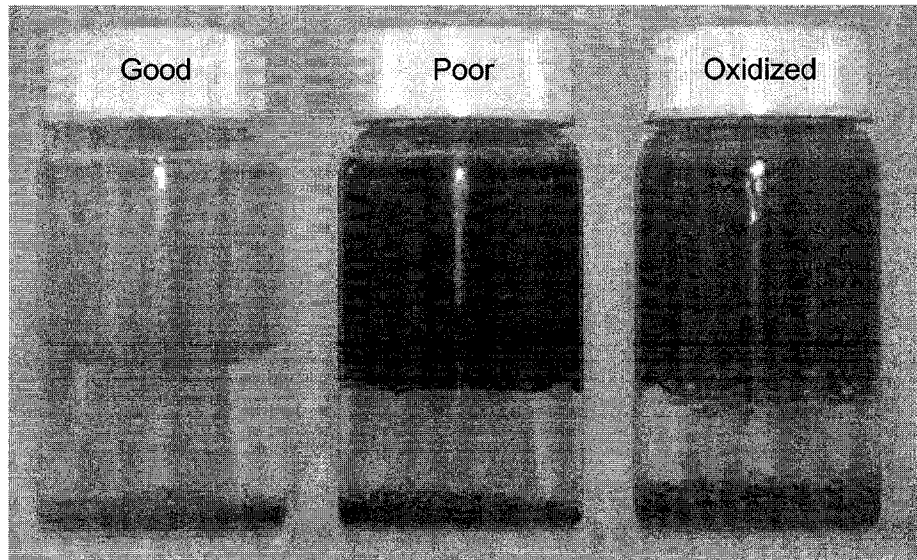


Figure 3.15: Visualization of partitioning of coarse solids in oil and water phase

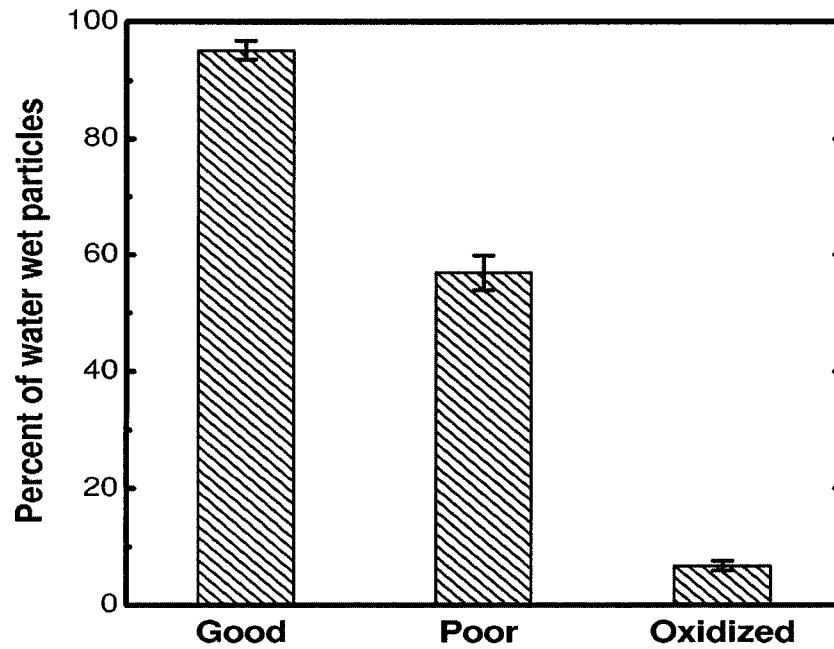


Figure 3.16: Percentage of the coarse solids from different oil sands in the water phase

Table 3.4: XPS results of the wet water washed coarse solids

Oil Sand Ores	Mass Concentration [%]					
	C	Si	S	Ca	Al	O
Good Processing	34.4	27.6	0.8	0.4	2.6	34.3
Poor Processing	51.6	17.8	1.9	0.6	2.8	25.5
Oxidized	65.9	14.3	3.1	0.1	0.3	16.2

hydrophilic [20]. The solids from the good processing ore had a higher percentage of Al and Si than the solids from poor processing and oxidized ores, supporting the results from the film flotation and indicating that the solids from good processing ores are more hydrophilic than those from poor processing and oxidized ores. These results support the finding that wet water washed coarse solids from good processing ores are more hydrophilic than the solids from poor processing and oxidized ores. The solids from the oxidized ores were most hydrophobic.

3.4.6 Water Drop Penetration Time for Fines

The time taken by a water drop to completely penetrate the compressed fines obtained from different ores can be an index for measuring the wettability of the fines. In soil science [14, 1], researchers use the water drop penetration time to characterize the water repellency of soil. The degree of water repellency can be measured by using water drop penetration time measurements.

Water drop penetration times were measured on compressed fines from good processing ores, poor processing and oxidized ores. To obtain a statistically representative value for the water drop penetration times, at least nine water drop penetration times were measured. The resulting data were then averaged. The standard deviation of the sample mean was calculated by assuming a t-distribution. The errors given are the 95% confidence limit. The values of the water drop penetration times for fines from different ores are tabulated in Table 3.5. The good processing ores had the shortest water drop penetration time whereas the oxidized ores had the longest water drop penetration time. The water drop penetration time for the poor processing ores lies between that of the good processing and oxidized ores. The values of the water drop penetration times suggest that the fines from oxidized ores are the most water-repellant (hydrophobic), in contrast to fines from good processing ores, which

Table 3.5: Water drop penetration time and initial contact angle of fine solids from different ores

Oil Sands Ores	Water Drop Penetration Time [s]	Initial Contact Angle[degree]
Good Processing (F11B)	4.5±0.7	32.4±0.5
Poor Processing (Posyn)	43.6±5.1	124.3±2.3
Oxidized (SunOxy)	161.4±2.6	126.5±4.1

are the least water repellent (hydrophilic).

The water drop penetration time test proved to be a good test for establishing the wettability differences among fine solids from ores.

3.4.7 Initial Contact Angles for Fines

The initial contact angle of the water drop on the compressed fines obtained from different ores was measured. The three-phase contact angle of the fines was measured in the water phase. To obtain a statistically significant value for the initial three-phase contact angles, at least nine initial contact angles were measured using different water drops on the samples. The resulting data were then averaged. The standard deviation of the population mean was calculated from the sample mean by assuming a t-distribution. The errors given are the 95% confidence limit. The initial contact angle values of the fines obtained from different ores are tabulated in Table 3.5.

Lower values for the contact angles imply hydrophilic fines, and higher values imply hydrophobic fines. The results in Table 3.5 show that initial contact angles were different for the fines solids from the good processing and other ores. The difference in the initial contact angles of fine solids from the oxidized ores and from poor processing ores lies inside the error limit. The initial contact angle measurements can not be used to differentiate the wettability of solids from the poor processing and oxidized ores. The initial contact angle values suggest that the fines from the good processing ores were hydrophilic whereas the fines from the poor processing and oxidized ores were hydrophobic.

3.5 Summary

The film flotation test and oil-water partitioning test results indicate that coarse solids from good processing ores are less hydrophobic than those from poor processing and oxidized ores. The solids from oxidized ore are the most hydrophobic among the three ore types. XPS analysis suggests that the presence of bitumen and surfactants on the surface may be responsible for these differences.

Film flotation also established that the solvent washing and drying of coarse solids affects the wettability of coarse solids.

The water drop penetration time test proved to be a good test to establish the differences among the fines from different ores. This test also established that the fines from the good processing ores were less hydrophobic compared to the solids from the poor processing and oxidized ores. The fines from the oxidized ores were the most hydrophobic.

In summary, the solids from oil sands are comprised of coarse and fine fractions. Both solid fractions were hydrophilic in the case of good processing ores. Solids were hydrophobic for the poor processing and oxidized ores.

Chapter 4

Relationship Between Processability and Wettability

In Chapter 2, the parameter called ultimate recovery was determined. The ultimate recovery parameter is used to estimate the processability of ores. In Chapter 3, different parameters were determined to characterize the coarse and fines solids from oil sands. The relationship between the processability of ores and the wettability of solids is investigated in this chapter.

The mean critical wetting surface tension of coarse solids from the different ores was used as a measure of the wettability of solids. The water drop penetration time was used as a parameter for characterizing the wettability of fines. The relationships between the wettability parameters of solids and the processability parameters are presented in this chapter.

4.1 Coarse Solids Wettability and Processability

Coarse solids were characterized by using two different techniques, the oil-water partitioning test and the film flotation test. The parameter obtained from the partitioning test was the percentage of solids in the water phase, while the film flotation test gave the mean critical wetting surface tensions of the coarse solids. Relationships were developed between these parameters and the ultimate bitumen recoveries.

The wet water washed coarse solids were used in the oil-water partitioning test. In this study WWWC was used because it was comparatively easier to obtain from oil sands.

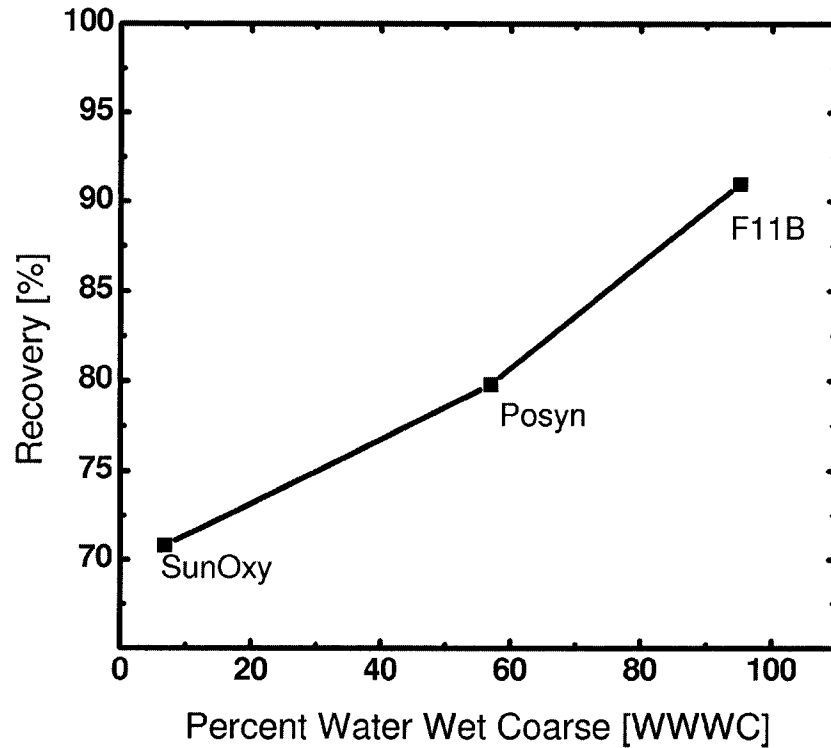


Figure 4.1: Relation between water wet coarse solids and recovery

Figure 4.1 shows the relationship between the oil-water partitioning test parameter (percentage of hydrophilic solids) and the ultimate recoveries from different oil sand ores. The x-axis represents the percentage of total solids remaining in the water phase, and the y-axis represents the ultimate recoveries of the different ores. Clearly, a good correlation exists between the percentage of solids in the water phase and the bitumen recovery from the oil sands. The bitumen recovery from the oil sands increased with an increase in the percentage of the total solids that were hydrophilic. The affinity of the solids towards bitumen increased with increasing hydrophobicity of the solids; hence liberating bitumen from the solids became relatively difficult. The result was a decrease in the bitumen recovery.

The film flotation test showed that the coarse solids from good processing ores were hydrophilic as compared to those from poor processing and oxidized ores. The coarse solids were washed with different solvents to assess the effect of washing on the wettability characteristic of the solids. The wet ethanol-washed solids showed a

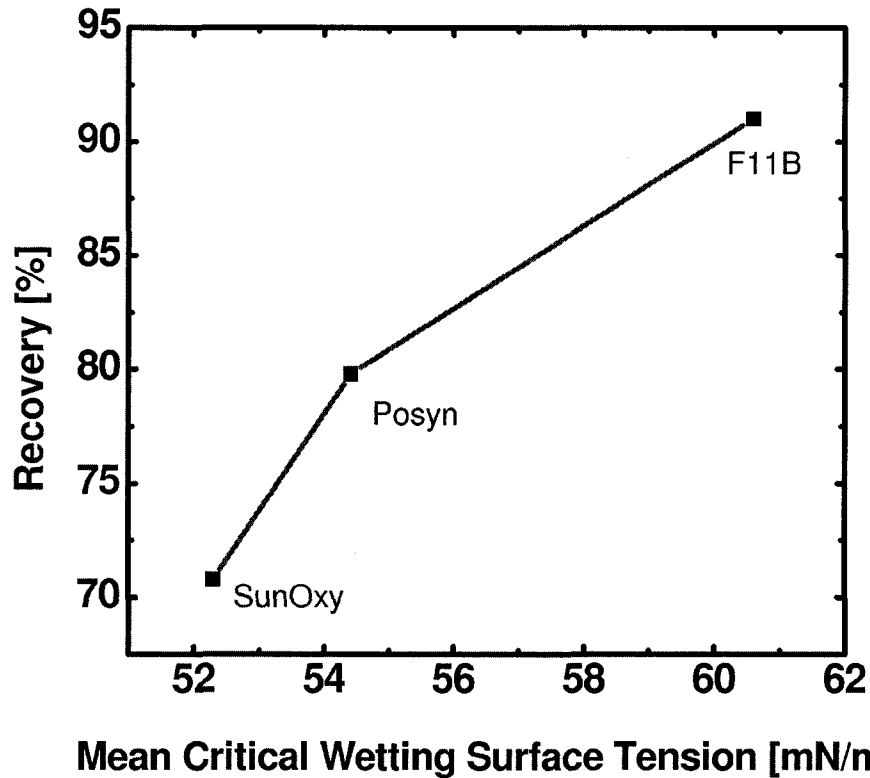


Figure 4.2: Relation between mean critical wetting surface tension of coarse solids and recovery

conspicuous difference in the wettability of the solids from different ores. It appears that the wet ethanol washing removed the surfactants that might have been adsorbed on the surfaces of the solids when dried, making the surface more exposed with silicon, oxygen, and other mineral components. As a result, the coarse solids became more hydrophilic. Due to this noticeable distinction, a mean critical wetting surface tension of the wet ethanol-washed coarse solids was used to establish a relationship with the ultimate bitumen recovery.

In Figure 4.2, the x-axis shows the mean critical wetting surface tensions of the coarse solids from the different ores, and the y-axis shows the corresponding ultimate recoveries of the ores. A strong correlation exists between the mean critical wetting surface tensions of the coarse solids and the ultimate recovery. The mean critical wetting surface tension of the solids increased with increasing hydrophilicity. The bitumen liberation became easier with increasing hydrophilicity of the coarse solids.

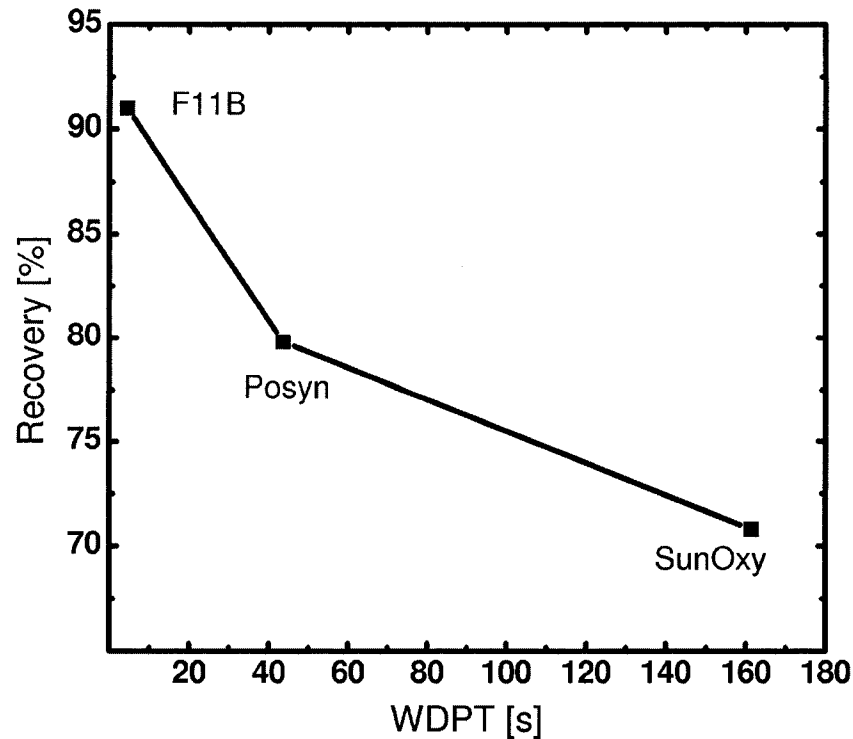


Figure 4.3: Relation between water drop penetration time of fine solids and recovery

4.2 Relation Between Fine Solids Wettability and Processability

Fine solids were characterized by the water drop penetration time and three-phase contact angles. Not much difference was observed, in terms of the contact angle of fine solids from the oxidized ores and poor processing ores, but the water drop penetration time showed a marked difference for the solids from these two ores and the good processing ores as well. Thus, the water drop penetration time was used as a parameter to characterize the fine solids wettability.

In Figure 4.3, the x-axis represents the average water drop penetration time of the fines from different ores and the y-axis represents the corresponding ultimate recoveries of the ores. This figure shows that the water drop penetration time of the solids decreased with increasing bitumen recovery; i.e., the higher the recovery of the ores, the lower the water drop penetration time of fine solids. Because the fines have a large surface area, comparatively more energy would be required to liberate bitumen

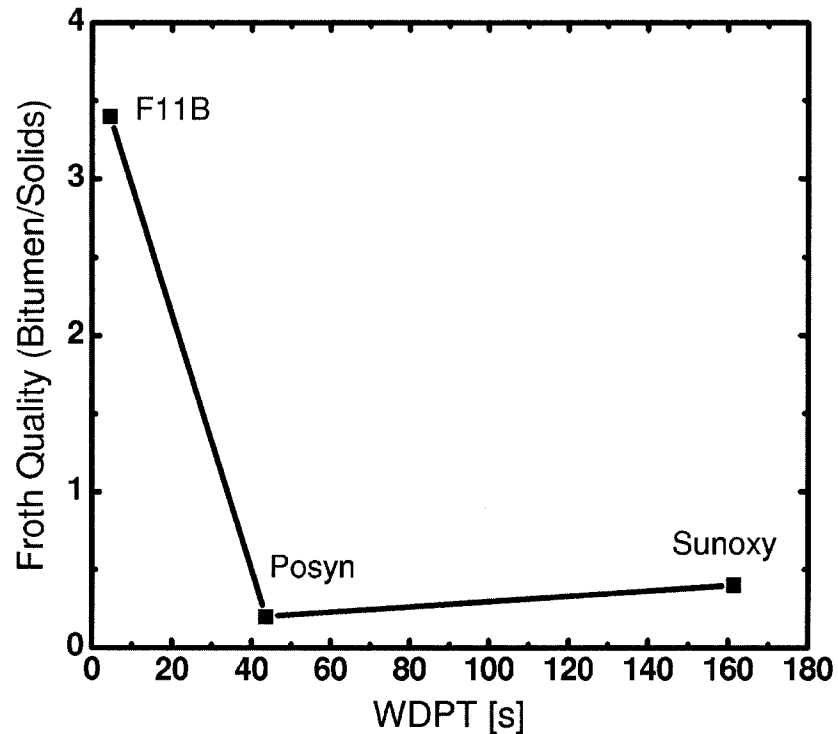


Figure 4.4: Relation between water drop penetration time of fine and froth quality or the ores

from the fine solids' surface, especially if the fines were hydrophobic in nature.

Recovery of bitumen not only depends on the percentage of bitumen recovered but also froth quality is important in determining the processability. Froth quality is defined as a ratio of bitumen to solids in froth. Poor froth quality indicates more solids in the bitumen. In general, fines solids get reported in the froth depending on its wettability. The results in graph 4.4 show, the variation of froth quality with the water drop penetration time of ores. Better froth quality was observed in case of good processing ores; whereas poor froth quality was observed in case of poor and oxidized ores. Fine solids from poor processing and oxidized ores being hydrophobic in nature, get attached to bubbles and hence report to the froth. In contrast fines from good processing ores hydrophilic in nature, causes fewer fines to attach to the bubbles leading to a good froth quality.

4.3 Summary

A strong correlation exists between the hydrophilicity of solids from different oil sands and the ultimate recoveries for the ores tested. Both the partitioning test and the film flotation test established that a strong correlation between the wettability of coarse solids and the processability of oil sands. The water drop penetration tests established a strong correlation between the wettability of fines and the processability of the ores.

Chapter 5

Quick Test for Processability

A jar test was developed to estimate the processability of ores. An attempt was made to estimate the differences among good processing, poor processing and oxidized ores by using jar tests. The visual assessment of the processability of oil sand ores was followed by quantitative determination of the processability of the ores.

5.1 Jar Tests for Processability

A measured amount of a oil sand ore was taken in a jar and mixed with a measured amount of de-ionized water. The sample jar was shaken in a shaker to allow phase separation.

Bitumen liberation from oil sands is affected by mechanical energy, temperature and solvent addition in the hot water extraction process [15, 16, 13]. The sensitivity of jar tests to temperature, mechanical energy and solvent addition was evaluated visually. The effect of mechanical energy on bitumen liberation in a jar test was tested by using mechanical shakers at room temperature. Different shaking speeds and shaking durations were tested. The effect of temperature on bitumen liberation in a jar test was evaluated by using temperature-controlled shakers. Three different temperatures were tested. Kerosene was used as a solvent to evaluate the effect of solvent addition on bitumen liberation from oil sands. Kerosene decreases the bitumen viscosity and hence helps in bitumen liberation [11]. In the entire set of tests, the bitumen liberation was first evaluated visually. If a difference in the bitumen liberation was observed, then further quantitative analysis was conducted.

The jar tests separated the oil sands and water mixture into three different layers.

The top layer contained primarily the liberated bitumen, some fines and very little water in emulsion form (water in oil emulsion). The middle layer contained primarily fines, water and some emulsified bitumen. The bottom layer contained coarse sand, unreleased bitumen and water containing fines. The oil sands having the higher percentage of bitumen on the top layer had better bitumen liberation as compared to the oil sands which had a lower percentage of bitumen on the top layer.

Jar-test sensitivity to temperature, mechanical energy and kerosene addition was tested to find the best method to distinguish among good processing, poor processing and oxidized ores.

5.2 Effect of Shaking Speed and Duration on Bitumen Liberation

The jar tests were carried out in a standard shaker (LINDBERG/BLUE) which had a water bath to control the temperature of the sample jars at a set temperature. The tests were performed at different shaking speeds (dial reading 10 was considered fast and dial reading 5 was considered slow) and shaking durations at room temperature to determine the effect of the shaking speed on bitumen liberation in jar tests.

A 20 g sample of oil sands was mixed with 40 g de-ionized water (pH 6.0-6.2). After mixing, the jars were left undisturbed for 20 minutes, and photos of the jars were taken. Two good processing, two poor processing and two oxidized ores were used for the tests. The characterization of the ores is presented in Table 2.2. Figure 5.4 shows a photograph of the jars. The jars were shaken at room temperature, with a fast shaking speed (dial reading: 10), and the shaking duration was set to 20 minutes. The green marker on the side of each jar in the photograph indicates the thickness of the upper layer (liberated bitumen) whereas the red marker on the side of the jar shows the thickness of the lower layer (un-liberated bitumen and solids). Figure 5.4 shows that with good processing ore, the bitumen was liberated and floats to the top, but this result was not observed with poor processing and oxidized ores. The thickness of the bottom layer was comparatively higher for the poor processing and oxidized ores. As very little bitumen liberation was observed in the poor and oxidized ores, no attempt was made to quantify the liberated bitumen. It was concluded that

at room temperature, it was not possible to distinguish the difference between poor processing and oxidized ores by using jar tests and varying the shaking speed and shaking durations.

5.3 Effect of Temperature on Bitumen Liberation

The jar tests at room temperatures showed a difference between the good processing and poor processing ores but were unable to show a difference between the poor processing and oxidized ores. Therefore, an attempt was made to assess the effect of temperature on bitumen liberation and to judge if a variation in temperature could establish a difference between the poor processing and oxidized ores.

A 20 g sample of oil sands at room temperature was mixed with 40 g of de-ionized water at 60° C in a 50 mL jar. The shaker was set to 50°C in order to conduct the experiment at the set temperature. Six jars containing two good processing, two poor processing and two oxidized ores were placed in the shaker and left undisturbed for 10 minutes in order to make the temperature of the oil sands and water mixture the same as that of the shaker temperature. Subsequently, the jars were shaken at maximum shaking speed for 20 minutes. Next, the jars were left undisturbed for the next 10 minutes to allow phase separation. A similar procedure was repeated with the water bath temperature set to 80° C. A difference in bitumen liberation was observed in the good processing ores when the temperature was increased from 50° C to 80° C, but not much difference in bitumen liberation was observed visually for the poor processing and weathered ores. Figure 5.2 shows the bitumen liberation at 80°C, fast shaking speed and 20 minutes shaking time. After observing the six jars visually, it was concluded that the bitumen liberation was not sensitive to temperature variation. Varying the temperature of the bath in the jar test did not result in an appreciable difference between poor processing and oxidized ores.

5.4 Effect of Kerosene Addition on Bitumen Liberation

The sensitivity of bitumen liberation to temperature and mechanical energy was discussed in the previous sections. The bitumen liberation in the jar test did not appear

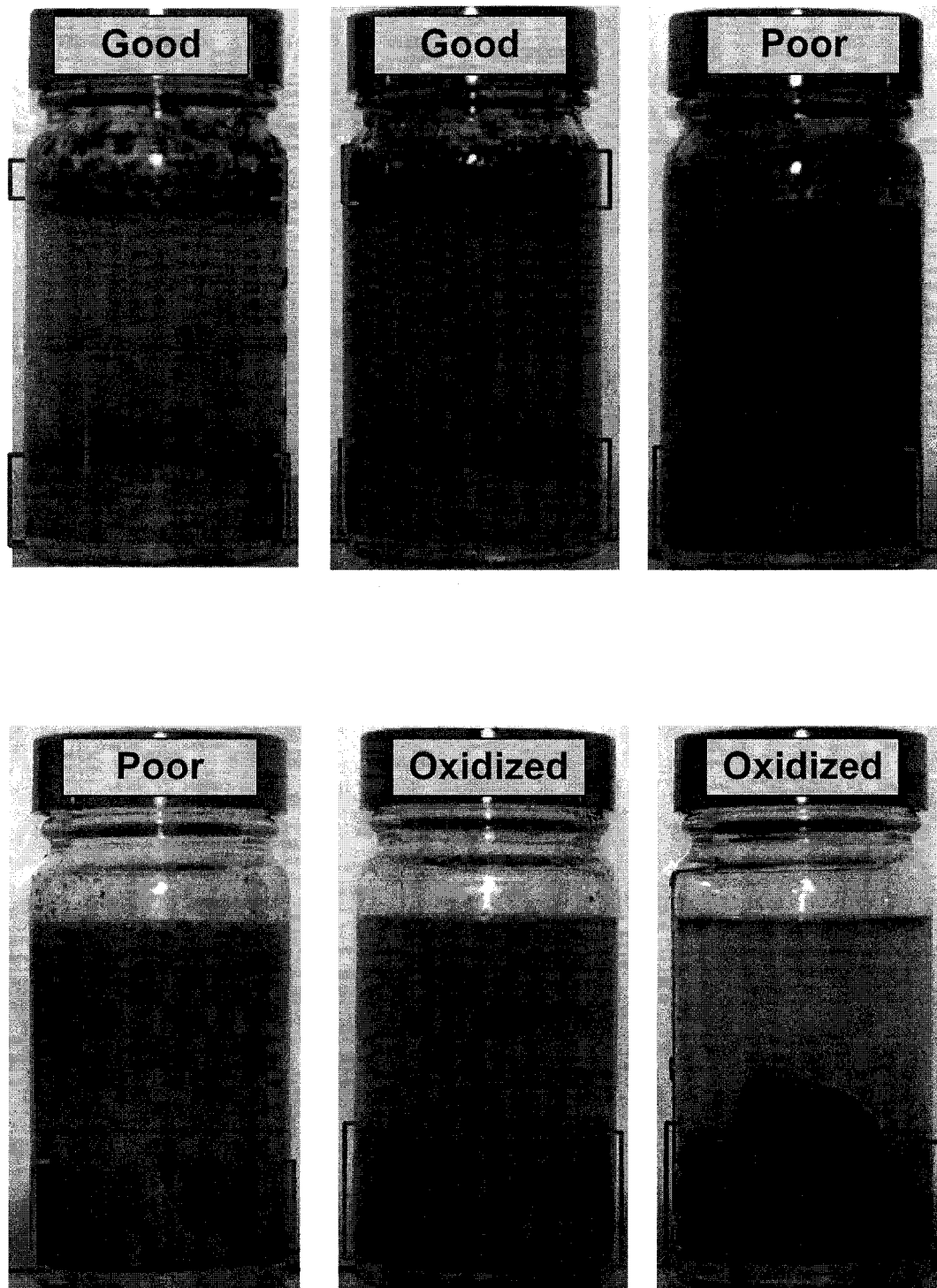


Figure 5.1: Visualization of bitumen liberation in jar test at room temperature, fast shaking speed for 20 minutes

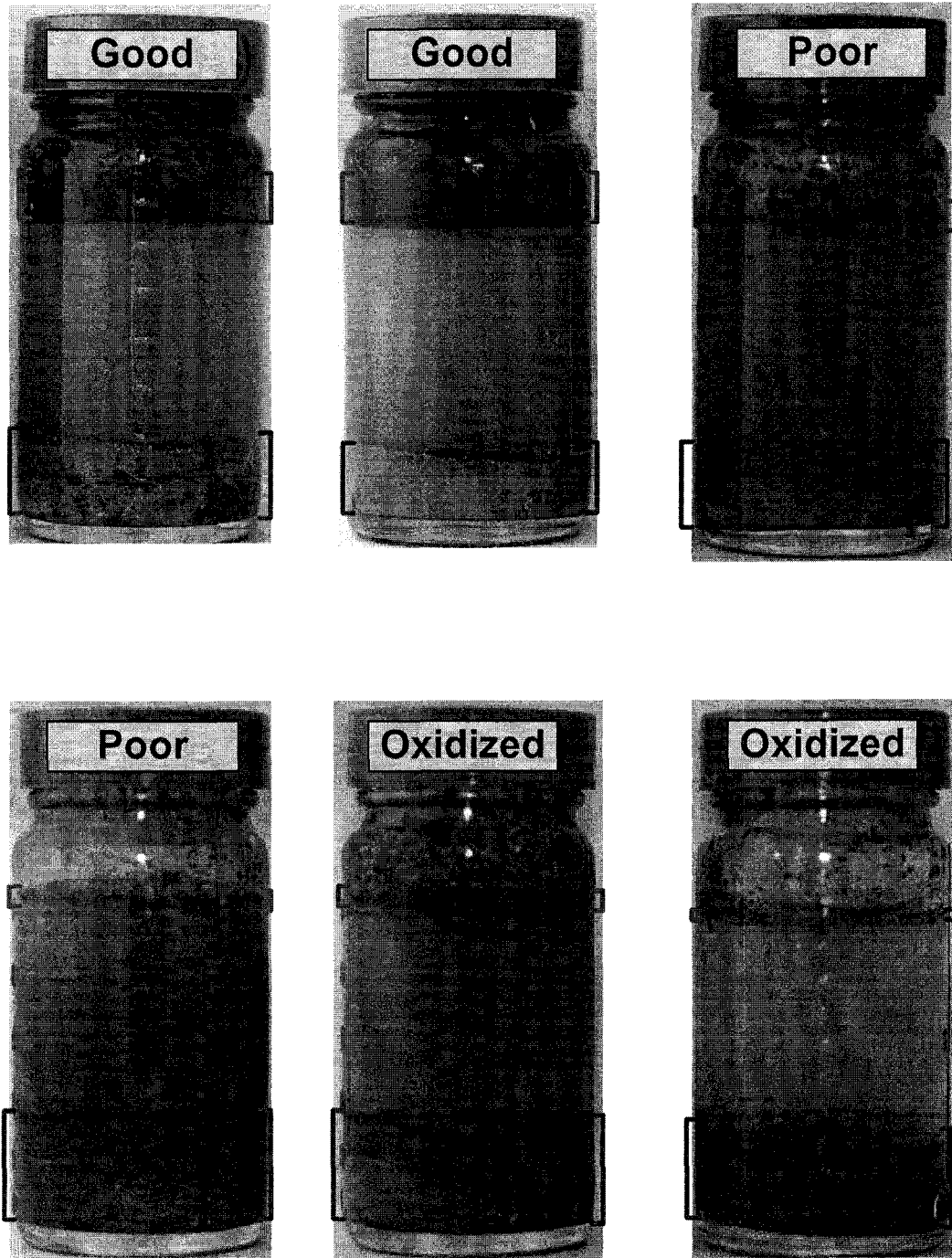


Figure 5.2: Bitumen liberation in jar test at 80°C, fast shaking speed for 20 minutes

to be sensitive to either of these variables. Next, the effect of adding kerosene was studied. A measured amount of kerosene was added to the water and oil sands mixtures and shaken in a standard shaker to study the effect of kerosene addition on bitumen liberation.

A 20 g sample of oil sands was mixed with 40 g de-ionized water (pH 6.0-6.2) in a 50 mL jar. Different amounts of kerosene were added to the oil sands and water mixtures, but the addition of 2 mL kerosene showed the best results in terms of visualization of bitumen liberation. The kerosene, water and oil sands mixture was shaken at a high speed setting in the standard shaker for 20 minutes and left undisturbed for 10 minutes to allow phase separation. This test was conducted at room temperature.

Figure 5.4 shows the visualization of the jar tests with the addition of 2 mL kerosene, room temperature, and a fast shaking speed for 20 minutes. Good bitumen liberation was observed. To obtain a clear visualization, the jars were left undisturbed for two weeks, and then photographs were taken. Clearly, kerosene addition improved bitumen liberation, and differences could be observed among the ore types. Therefore, a further investigation was conducted to find a standard test procedure to conduct jar tests. Once the visualization experiment showed a positive result, further quantitative assessment of bitumen liberation was conducted.

To estimate the quantitative amount of bitumen released from oil sands, the top layer was scooped out, and 250 mL of toluene was added. The mixture was centrifuged at 2000g to separate the solids from the solution. Five mL of the centrifuge sample was extracted in a graduated pipet. The bitumen solution was uniformly spread on the pre-weighed filter paper. The filter paper was hung for 30 minutes in a fume hood to allow complete evaporation of the toluene. The bitumen remained on the filter paper, and the dried filter paper was then weighed. The weight of the bitumen in the 5 mL sample was determined by subtracting the clean filter paper weight from the weight of the filter paper with the bitumen. Multiplying it by 50 gave the bitumen content of the top layer. The middling water was decanted carefully, and its pH was measured. The bottom layer was dried in an oven overnight to allow the complete evaporation of water. The procedure described above was repeated to determine the bitumen content in the bottom layer. Adding the bitumen content measured in the

top and bottom layers gave the approximate value of the total bitumen in the original oil sands. The percentage of bitumen in the top layer was calculated, and the result was called the jar test recovery.

5.5 Proposed Jar Test Procedure

The experiments discussed earlier refined the jar test procedure until it could distinguish among the three types of ores. Thus, a standard test method is now proposed for the jar test to quantify the bitumen liberated. The fraction of bitumen floating on the top layer is termed as the jar test recovery.

5.5.1 Materials

Oil sand ores, de-ionized water, kerosene, filter paper, and toluene.

5.5.2 Apparatus

Standard shaker(LINDBERG/BLUE), jars, pipettes, and beakers.

5.5.3 Procedure

1. Put a 20 g sample of oil sands into a 50 mL glass jar.
2. Add 40 g of de-ionized water and 2 g of kerosene to the oil sands at room temperature.
3. Shake the jar in a standard shaker for 20 minutes.
4. Leave the jar undisturbed for 10 minutes in the upright position.
5. Take photographs for visualization of layer separation.
6. Scoop the top layer by using a spatula into a beaker, and add 250 mL toluene into the beaker.
7. Put the bitumen and toluene mixture in a 50 mL centrifuge tube and Centrifuge the solution at 2000g for 20 minutes to remove the solids from the solution.

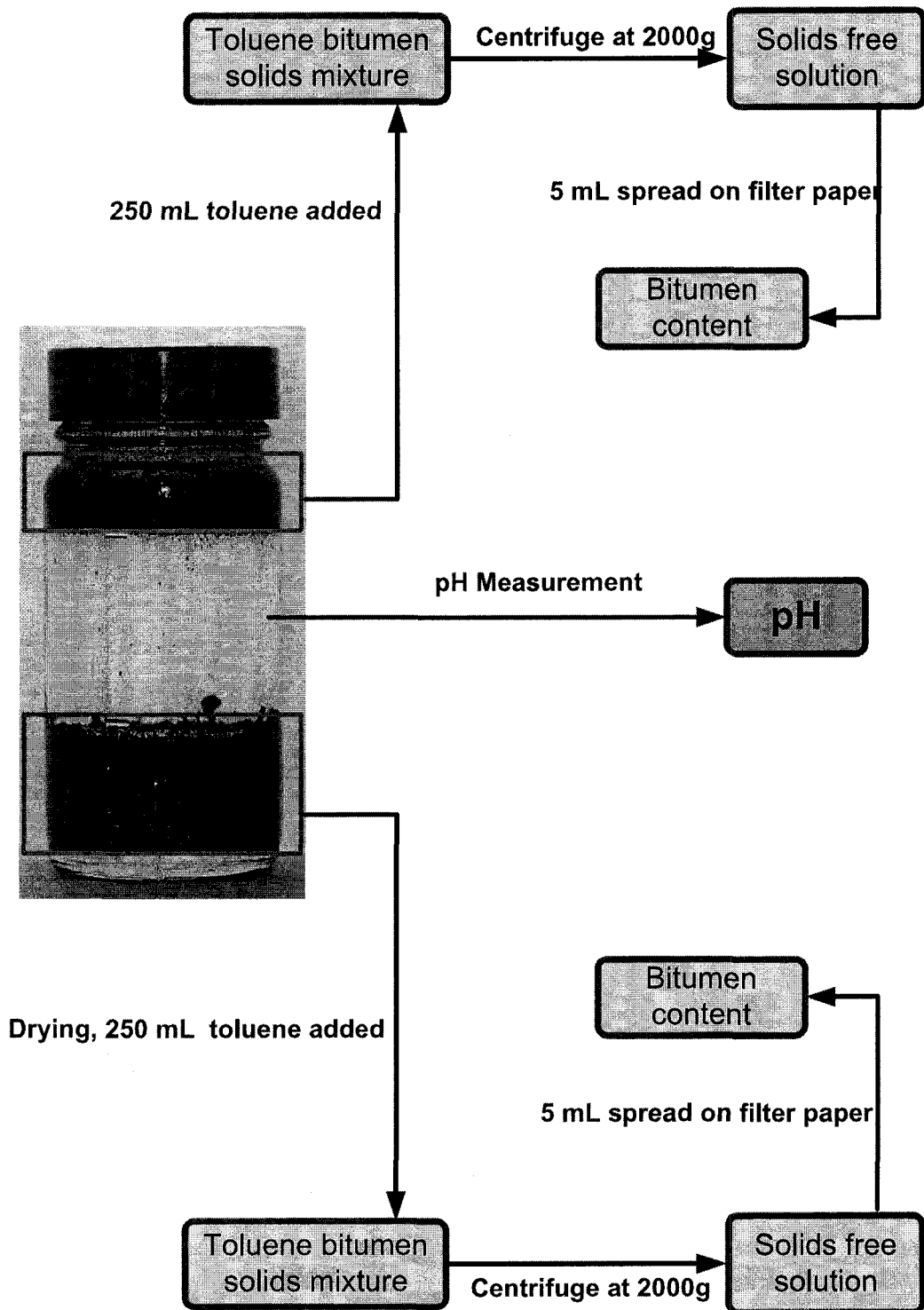


Figure 5.3: Jar test to estimate processability

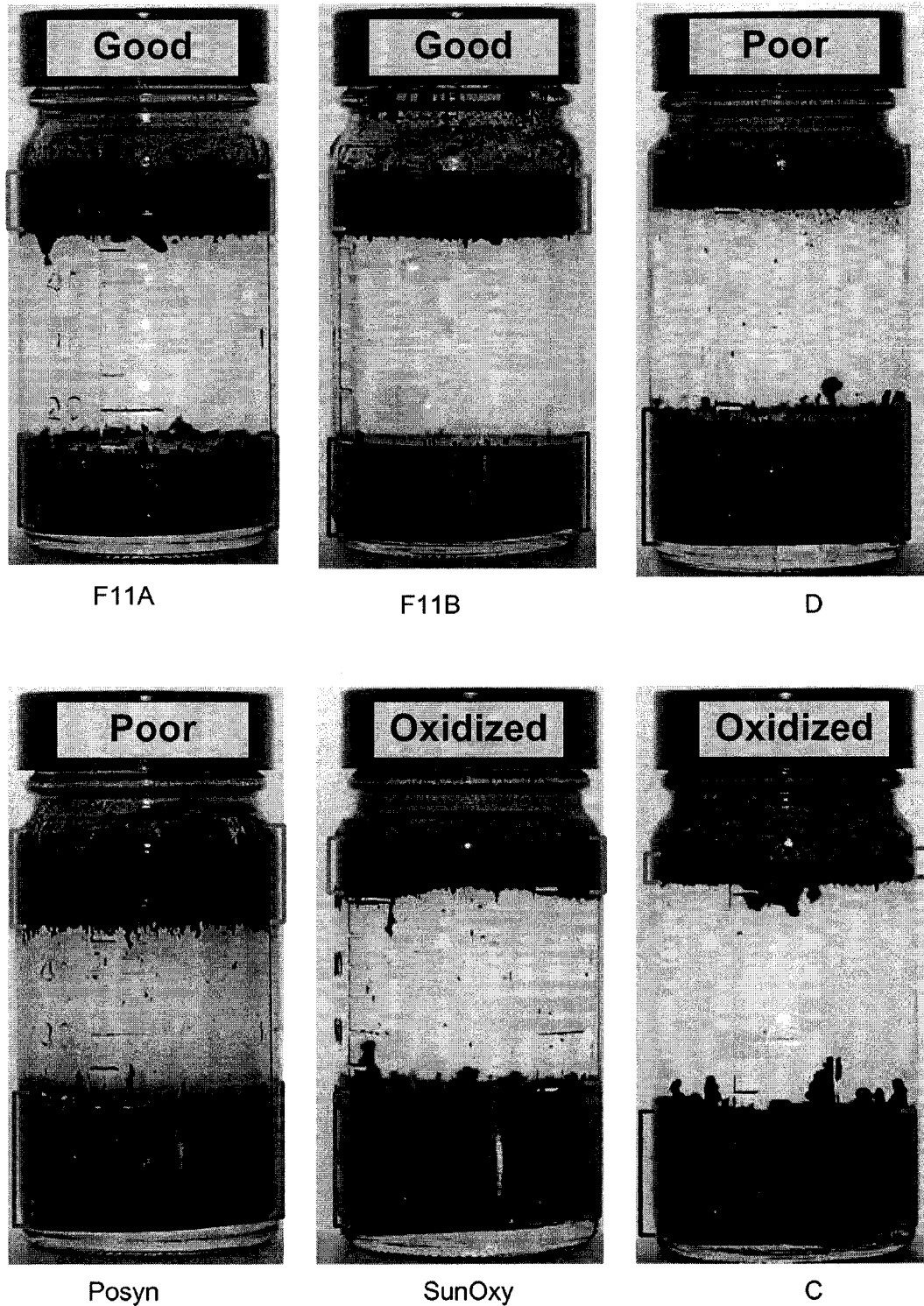


Figure 5.4: Bitumen liberation in jar test at room temperature, fast shaking speed (dial reading=10) for 10 minutes with kerosene addition

8. Take a 5 mL sub sample of the centrifuged toluene and bitumen solution, and spread it on the pre-weighed filter paper by using a pipette.
9. Dry the filter paper, and weigh it to determine the amount of bitumen on the filter paper.
10. Decant the middle layer water, and measure the pH of the middling water to see if the pH can be used to distinguish between the among ore types.
11. Keep the remaining bottom layer in an oven at 120 °C overnight to dry the remaining water.
12. Add 250 mL toluene to the bottom layer; mix and transfer the bitumen toluene solution into a 50 mL centrifuge tube.
13. Centrifuge the bitumen toluene solution at 2000g for 20 minutes to remove the solids.
14. Take a 5 mL sub-sample of the centrifuged toluene and bitumen solution and spread it on the pre-weighed filter paper by using a pipette.
15. Dry the filter paper, and weigh it to determine the amount of bitumen on the filter paper.

5.6 Results and Discussion

Observing the photographs of the different jar tests led to the conclusions that bitumen liberation is sensitive to kerosene addition in the jar tests. Bitumen liberation was observed even in the poor processing and oxidized ores. The photographs show that the thickness of the upper layer of bitumen is very similar for the good processing and poor processing ores. This observation can be misleading. Visually, it would appear that the recovery in the poor processing ores is the same as that in good processing ores. In the bottom side of the upper layer of the poor processing ores, long dendrite-like structures could be seen. They were present because the top bitumen layer was loaded with fines, which were trying to fall to the bottom layer

due to gravity. Therefore, the dendrite-like structures on the top layer of the poor processing ores could indicate high fines in these ores.

The poor processing ores and oxidized ores could be easily distinguished by measuring the pH of the middle layer. This pH varied from 7 to 8 for the good processing and poor processing ores, whereas the pH of the oxidized ores varied from 5 to 6. The oxidized ores' mid layer showed a typical weak acidic nature, and the poor processing and good processing ores middle layers showed a typical basic nature. Therefore, the pH of the middle layer could be used as a variable to distinguish between oxidized and other kinds of ores.

The kerosene addition showed promising results, so the quantitative value of the bitumen liberated from the oil sand was assessed by using the method shown in Figure 5.3. The recovery from the jar tests was compared with that from the standard Denver flotation tests to prove that the jar test recovery was comparable to the standard Denver flotation recovery. Figure 5.5 shows the comparison between the jar test recovery and Denver flotation tests. The graph shows a direct relation between Denver flotation recovery and jar test recovery. As the recovery of the ores increased in the Denver flotation, the jar tests recovery also increased. This finding indicates that a jar test with kerosene addition can be used as a quick test for processability assessment.

5.7 Summary

Visual observations showed that the jar test is not sensitive to the shaking speed, shaking time and temperature of the jars. The jar test with kerosene addition proved to be a good test to assess the processability of the ores. This test can be used as a quick and easy test to estimate ore processability.

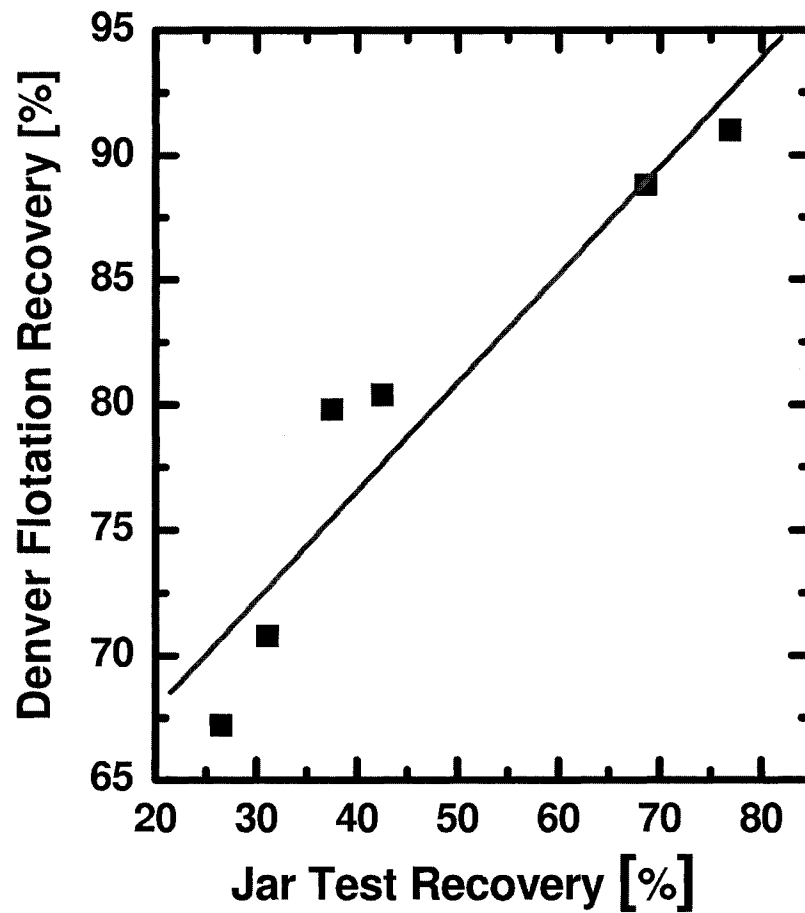


Figure 5.5: Comparison of Jar test recovery with Denver cell recovery

Chapter 6

Conclusions and Recommendations

6.1 Conclusions

The main goals of the research were to study the wettability of solids extracted from different oil sands. Both coarse and fine fractions were studied by using different techniques. Suitable techniques for characterizing the solids wettability were recommended. Using these techniques, relationships between oil sands processability and solids wettability were established. Another objective of the research was to develop an easy test to estimate the processability of the ores.

Six different kinds of ores were chosen from a range of ore types that were available for testing. Standard Denver flotation experiments were used to classify and group the ores into three different categories: good processing, poor processing, and oxidized or weathered ores. Good processing ores had high bitumen content, low percentage of fines in the solids fraction, and relatively low electrolyte content of the ores. Good processing ores also had high ultimate recovery as well as a high initial bitumen flotation rate. Poor processing ores had low bitumen content, high fines content, and high electrolyte content of the ores. Poor processing ores also had a lower ultimate recovery and initial flotation rate from the Denver floatation test. The oxidized (or weathered) ores had similar properties as those of the good processing ores, except that the pH of the ores and distilled water mixture were in the acidic range (pH 5-6) and had low recovery.

Wettability characterization of the solids extracted from the three types of oil sands was conducted by using different techniques. The solids were extracted from the oil sands by using the Denver flotation water-based extraction process. The

extracted solids were split into coarse and fine fractions. The coarse fraction of the solids was characterized by using film flotation experiments and oil-water partitioning tests. The fine fraction of solids was characterized by using a water drop penetration time test and an initial contact angle measurement test.

The coarse solids were washed with different solvents to find a suitable washing procedure that could be used to distinguish the three kinds of ores. The effect of solvent washing on the wettability characteristic was studied by using the film flotation technique. The same technique was used to study the effect of drying on solids' wettability.

The dried coarse solids from the different ores were washed with toluene, ethanol and ethanol-toluene to establish the effect of solvent washing on the coarse solids wettability. The solids from an ore became progressively more hydrophilic when washed with toluene, ethanol and ethanol-toluene. The toluene dissolved the bitumen from the solids' surface, making the solids comparatively more hydrophilic. It is suspected that ethanol washing dissolved the adsorbed surfactants from the surface of the solids, hence making the solids more hydrophilic. When the coarse solids were washed with both ethanol and toluene, the solvents washed both the bitumen and surfactants from the solids' surface, making the solids the most hydrophilic.

The effect of drying on the wettability of solids was studied by washing the coarse solids with ethanol when the solids were wet and washing the solids after drying. It was found that the coarse solids were more hydrophobic when washed after drying.

The coarse solids from the good processing, poor processing and oxidized ores were, in sequence, increasingly hydrophobic, independent of the washing procedure that was adopted. The wet coarse solids washed with ethanol showed a marked difference in the wettability of the coarse solids from the different ores. Therefore, if the goal is to distinguish ore types by their solids wettability, the recommended washing procedure is to wash the solids with ethanol while the coarse solids are still wet. The oil-water partitioning tests indicated that the coarse solids from the good processing ores, poor processing and oxidized ores were increasingly hydrophobic.

The XPS results of the coarse solids from the three ore types showed differences in terms of the elemental compositions of the solids' surface. The oxidized ores showed a high percentage of sulphur elements, which can explain the acidic nature of the ore.

The amount of carbon on the surface of the coarse solids from the good processing ores was lowest compared to that of the other ores types. The oxidized ores had the most carbon on the surface of the solids. The presence of carbon on the surface of the solids can explain the hydrophobic nature of these coarse solids.

The wettability characterization of the fines was conducted by using initial contact angle measurements and water drop penetration time tests. Initial contact angle measurements were able to distinguish differences in the wettability characteristics of the fines from the good and poor processing ores, but were unable to distinguish the difference between fines from the poor processing and oxidized ores. The water drop penetration time test proved to be a better test to differentiate among the three types of ores. Therefore, the water drop penetration time test is recommended when studying the wettability of fines from different ores.

Different wettability tests gave different wettability indices, which were correlated with the ultimate bitumen recovery from the ores. The mean critical wetting surface tensions were obtained by using the film flotation technique. The mean critical wetting surface tensions of the coarse solids had a positive correlation with the processability of the ores; i.e., as the solids became more hydrophilic, the recovery of the bitumen increased. Similar conclusions were found by using the oil-water partitioning tests and the water drop penetration time.

A jar shaking test was developed for the quick assessment of oil sands processability. The bitumen liberation in the jar shaking test was not very sensitive to the temperature, shaking speed and shaking time, but the addition of a small amount of kerosene increased the amount of bitumen liberated. The results from the jar shaking test also showed a good correlation with the standard Denver flotation recovery.

6.2 Recommendations for Future Testing

- The wettability of the solids (coarse and fine fractions) should be measured and correlated with processability of oil sands because the wettability of solids have a direct impact on the ease at which bitumen is liberated from the solids.
- Wet coarse solids washed with ethanol should be used to prepare specimens for film flotation tests. This preparation technique improves the ability of the

film floatation test to distinguish the different wettability characteristics of the solids obtained from different types of oil sands ores.

- The water drop penetration time test can be used to assess and distinguish the wettability characteristics of the fines from different ores.
- Jar shake tests with a small amount of kerosene added to the oil sands can be used as a quick visual processability assessment.
- Film floatation apparatus should be automated and developed further to characterize fines solids.
- A larger number of samples from a wide range of ores should be used to determine the validity of relationship between processability of ores and its solids wettability.
- Attempts should be made to characterize solids from froth
- Toluene washing procedure should be applied to extract solids directly from ores for further wettability study of solids
- A scaled down bottle tests should be tried to extract solids from oil sands

Bibliography

- [1] U. Buczko and O. Bens. Assessing soil hydrophobicity and its variation through the soil profile using two different methods. *Soil Science Society American Journal*, 70:718–727, 2006.
- [2] J. Bulmer and J. Starr. *Syncrude Analytical Methods For Oil Sand and Bitumen Processing*. AOSTRA, 1989.
- [3] K. Clark. Hot-Water Separation of Alberta Bituminous Sand. *The Canadian Institute of Mining and Metallurgy*, pages 251–214, 1994.
- [4] Fine Tailings FUNDamentals Consortium. Advances in oil sands tailings research. *Alberta Department of Energy, Oil Sands and Research Division*, 1:5–7, 1995.
- [5] D. Fuerstenau, J. Diao, and J. Hanson. Estimation of the distribution of surface sites and contact angles on coal particles from film flotation data. *Energy and Fuels*, 4(34-37), 1990.
- [6] D. W. Fuerstenau, J. Diao, and M. C. Williams. Characterization of the lyophobicity of particles by film flotation. *Colloids and Surfaces*, 22:87–91, 1987.
- [7] D. W. Fuerstenau, J. Diao, and M. C. Williams. Characterization of the wettability of solid particles by film flotation 1. Experimental investigation. *Colloid and Surfaces*, 60:127–144, 1991.
- [8] D. W. Fuerstenau and M. C. Williams. A new method for characterization of the surface energy of hydrophobic particles. *Particle Characterization*, 4:7–13, 1987.
- [9] D. W. Fuerstenau, M. C. Williams, K. S. Narayanan, J. L. Diao, and R. H. Urbina. Assessing the wettability and degree of oxidation of coal by film flotation. *Energy and Fuels*, 2:237–241, 1988.
- [10] G. Hepler and G. Russell. *The Alberta Oil Sands: Industrial Procedures for Extraction and Some Recent Fundamental Research*. 14. AOSTRA Technical Publication, 1994.
- [11] J. Hupka, J.D. Miller, and J. Drelich. Water based bitumen recovery from diluent conditioned oil sands. *The Canadian Journal of Chemical Engineering*, 82:978–985, 2004.
- [12] T. Kasongo, Z. Zhou, Z. Xu, and J. Masliyah. Effect of clays and calcium ions on bitumen extraction from Athabasca oil sands using flotation. *The Canadian Journal of Chemical Engineering*, 78:674–681, 2000.
- [13] J. Liu, Z. Xu, and J. Masliyah. Processability of oil sand ores in Alberta. *Energy and Fuels*, 19:2056–2063, 2005.

- [14] W. Louis and J. Coen. How water moves in a water repellent sandy soil 1. Potential and actual water repellency. *Water Resource Research*, 30:2507–2517, 1994.
- [15] J. Masliyah. *Intensive Short Course on Extraction of Oil Sands Bitumen*. Department of Chemical and Materials Engineering, University of Alberta, Edmonton, 2000.
- [16] J. Masliyah, Z. Zhou, Z. Xu, J. Czarnecki, and H. Hamza. Understanding water-based bitumen extraction from Athabasca oil sands. *The Canadian Journal of Chemical Engineering*, 82, 2004.
- [17] E. Sanford and F. Seyer. Processibility of Athabasca tar sand using a batch extraction unit: The role of NaOH. *CIM bulletin*, pages 164–169, 1979.
- [18] L. Schramm and R. Smith. Some observations on the aging phenomenon in the hot water processing of Athabasca oil sands. Part 1 The nature of the phenomenon. *AOSTRA Journal*, 3:195–215, 1987.
- [19] L. Schramm and R. Smith. Some observations on the aging phenomenon in the hot water processing of Athabasca oil sands. Part 2 The mechanism of aging. *AOSTRA Journal*, 3:215–224, 1987.
- [20] B. Sparks, L. Kotlyar, J. Carroll, and K. Chung. Athabasca oil sands: Effect of organic coating solids on bitumen recovery and quality. *Journal of Petroleum Science and Engineering*, 39:417–430, 2003.
- [21] Z. Xu. *Custom Courseware of Fundamental of Oil Sands Extraction*. Department of Chemical and Materials Engineering, 2006.
- [22] Z. Zhou, T. Kasongo, Z. Xu, and J. Masliyah. Assessment of bitumen recovery from the Athabasca oil sands using a laboratory Denver flotation cell. *The Canadian Journal of Chemical Engineering*, 82:696–703, 2004.