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Distribution of Oil Sands Formation Water in Bitumen Froth

by

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Abstract

Bitumen froth from oil sands extraction typically contains 60 wt.% bitumen, 30 wt.% water, and 10 wt.% solids. To meet downstream process specifications, the water and solids in bitumen froth have to be removed. The objective of this study is to identify the source of the water reporting to the bitumen froth. The water comes from two sources: formation water contained in mined oil sands ore, about 3-7 wt.%; and processing water added during the extraction process to recover bitumen from oil sands. Determining the distribution of the formation water will enable us to go one step further to understand the effect of formation water on water removal from bitumen froth.

After Denver Cell flotation process, the electrical conductivity of the emulsified water, free water and tailings water was determined. The results showed that the conductivity of emulsified water was higher than other water samples, indicating that high salinity formation water preferentially reported to the bitumen froth.

To better differentiate distribution of formation water among various process streams, oil sands extraction was carried out using heavy water instead of normal water as processing water, the density of collected water samples was measured by high precision density meter. However, no conclusive result could be obtained by this method.

To obtain more accurate quantification of formation water distribution, cobalt as chemical tracer was introduced in the processing water. Following the same procedure of oil sands extraction and water samples collection as in conductivity measurement

and heavy water density measurement, the concentration of cobalt in various product streams was determined accurately by Atomic-Absorption spectroscopy. The percent of formation water in emulsified water was then calculated.

To understand formation water distribution in the context of oil sands ore characteristics, different types of ores were tested. The results showed that the characteristics of an oil sands ore were decisive factor determining formation water distribution. It appeared that preferential distribution of formation water in the bitumen froth was detrimental to froth treatment.

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Chapter 1: Introduction

1.1 Oil sands overview

Oil sands, also known as tar sands, or extra heavy oil, are a type of bitumen deposit. Alberta has huge deposits of oil sands containing an estimated 1.7 to 2.5 trillion barrels of crude oil, making Canada the second largest oil reserves only after the Saudi Arabia reserves (Oil and Gas Journal, 2005). These deposits covering 140,200 square kilometers (54,132 square miles) of the province are located in three main regions: Peace River, Athabasca (Fort McMurray area) and Cold Lake (north of Lloydminster). The Canadian oil sands were formed about 50-100 million years ago, when crude oil was released from shale under the Rocky mountains and migrated eastward and upward into sedimentary sand deposits in eastern Alberta. The crude oil went through cold metamorphism, such as microbe biodegradation, volatilization of light hydrocarbons, aqueous wash and oxidation, removing low-molecular weight paraffin hydrocarbon components and enriching polar heteroatom complexes that made up the dense and viscous bitumen.

Oil sands contain 7-13 wt.% bitumen, 3-7 wt.% water, and 80-85 wt.% mineral solids. As a product of the oil sands, bitumen requires to be upgraded to synthetic crude oil or diluted with lighter hydrocarbons to make it transportable by pipelines to refineries. At room temperature, the viscosity of bitumen is usually much higher than 1.0×10^4 mPa·s, the specific gravity is greater than 1.0, and it contains relatively high level of heavy metals.

1.2 Bitumen production process

Since the first European saw the Athabasca oil sands, extensive efforts have been made to achieve economic development for oil sands industry. G. Hoffman (1883) working for the Geological Survey of Canada was one of the pioneers who attempted to separate bitumen from oil sands by water. Sidney Ells (1913) employed by the Federal Department of Mines advocated the hot water flotation method and conducted a number of experiments to test this technique. He was the first to bring out samples from the area for laboratory testing to pave 600 feet of road in Edmonton, Alberta, which lasted for 50 years. Dr. Karl Clark, a scientist with the Alberta Research Council in the 1920s, conducted experiments with a hot water flotation process which involved mixing oil sand with hot water and aerating the resultant slurry. The hot water flotation method is still the basis of the current commercial extraction processes of mined oil sands industry. (Source: Syncrude Fact Book, 2009)

Commercial production of bitumen from mined oil sands began in 1967, when Great Canadian Oil Sands Limited opened its first mine. Development was inhibited by declining world oil prices. The second mine, operated by the Syncrude consortium, did not begin its commercial production until 1978. Although the 1979 energy crisis caused oil prices to peak again, introduction of the National Energy Program by Pierre Trudeau discouraged foreign investment in the Canadian oil industry. During the 1980s, oil prices declined to very low levels, causing considerable retrenchment in the oil industry. The third mine, operated by Shell Canada, did not begin until 2003. As a result of oil price increases since 2003, the existing mines have been greatly expanded and new ones are under planning. The global economic recession set back again the entire oil sands industry because relative low oil prices since the end of 2008. The newest oil sands producer, Canadian Natural Resources Limited started its operation in spring 2009.

Oil sands mining: Oil sands ore is obtained by open pit mining for deposits buried less than about 50 meters. Large scale shovels and trucks are used to remove overburden and expose the oil sands ore. For in-situ production of bitumen from ore body below 100 meters, various techniques can be used. One technique is steam-assisted gravity drainage (SAGD). In SAGD, steam is added to the oil sands formation using a horizontal well to heat up the formation and hence reduce viscosity of bitumen. The heated bitumen is pumped above ground using a second horizontal well located below the steam injection well. SAGD operations can recover as much as 55% of the bitumen in-place (Deutsch and McLennan, 2005). Another technique called the Vapor Extraction Process (VAPEX) operates similarly to SAGD. But instead of steam, ethane, butane or propane is injected into the reservoir to mobilize the hydrocarbons toward the production well. This method requiring no steam in processing is 25% lower in capital costs and 50% lower in operating costs than the SAGD process.

The basic bitumen extraction process from the mined oil sands consists of following several steps.

Oil sands ore preparation: The mined ore lumps are crushed and mixed with hot water to form slurry in mixing boxes, cyclo-feeders or rotary breakers. In order to liberate bitumen from the sands grains, the slurry is then pumped through a hydrotransport slurry pipeline. In some operations, air is injected into the slurry pipeline where bitumen droplets are allowed to attach to air bubbles.

Bitumen extraction: The aerated slurry is pumped into a gravity separation vessel, where the slurry is separated into primary bitumen froth, middlings and tailings. The primary froth normally contains 60 wt.% bitumen, 30 wt.% water and 10 wt.% fine solids by weight. The middle stream from the vessel called middlings containing unrecovered small bitumen aggregates is re-aerated in flotation cells to allow more bitumen to float to the surface of the pulp as secondary bitumen froth.

Froth treatment: The bitumen froth from gravity separation vessels or flotation cells is generally de-aerated by steam. Diluents are then added to reduce the viscosity and density of bitumen in the froth to further separate it from water and solids. The treated bitumen after naphthenic froth treatment still contains 1.5-2.5 wt.% water (0-100 ppm for paraffinic treatment) and 0.4-0.8 wt.% solids (500-800 ppm for paraffinic treatment) (Canadian Heavy Oil Association, 2004).

Tailings management: Tailings from the separation vessels and flotation cells are pumped into large tailings ponds. After formation of the mature fine tailings, coarse solids from process tailings are mixed with MFT and gypsum to form non-segregating consolidated tailings, thereby releasing water for recycle to the extraction process.

Bitumen upgrading: Upgrading involves thermal treatment and coke rejection while adding hydrogen to make more valuable hydrocarbon products. This is done using four main processes: thermal treatment breaks large bitumen molecules into smaller fragments, distillation separates hydrocarbon molecules into their boiling point components, catalytic conversion helps transform hydrocarbons into more valuable products, and hydrotreating is used to remove sulfur and nitrogen and increase hydrogen to carbon ratio in the product. The end product of upgrading is the synthetic crude oil, SCO, which is shipped by underground pipelines to refineries across North America, where it is refined further into jet fuels, gasoline and other petroleum products.

A generic flow diagram of oil sands mining to bitumen upgrading is shown in Figure 1-1:

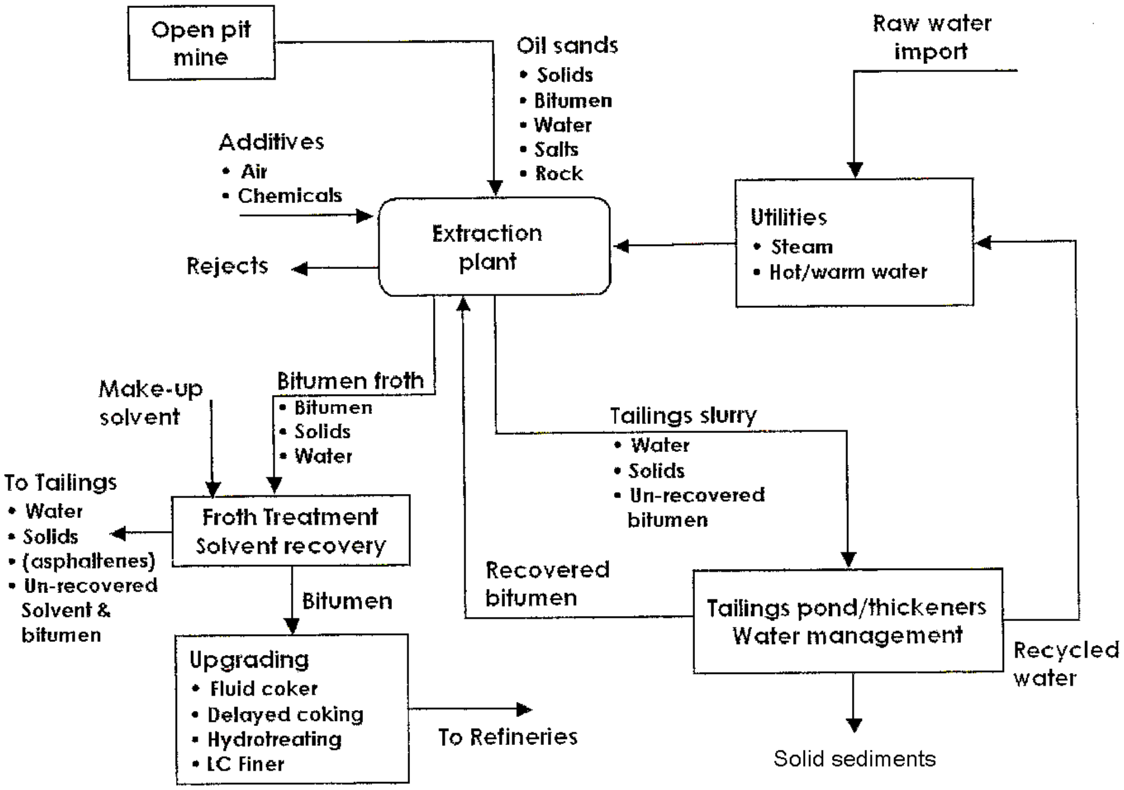

Figure 1-1: Generalized scheme for oil sands processing (Masliyah, 2004)

1.3 Objective of thesis

Stable water-in-oil emulsions are undesirable due to corrosions in upgrading and refining of bitumen. The emulsions must be treated to remove the dispersed water droplets and associated fine solids to meet the requirements for the downstream upgrading processes, which is less than 0.5 vol.% of total water and solids.

The water in bitumen froth could come from two sources: formation water (connate water) contained in oil sands ore, about 3-7 wt.%; and the added processing water in the bitumen extraction process to recover bitumen from oil sands. The formation water in the oil sands is of high salinity which can be at similar level as seawater. The sodium and chloride ion concentrations can vary from 10-100 mg/kg of oil sands. Calcium and magnesium ions can vary up to 40 mg/kg of oil sands (Masliyah, 2007). Other inorganic ions (e.g. K^+) are also present in the formation water. The process water used in bitumen extraction processes contains dissolved ions from common salts of sodium, magnesium, calcium, chloride and sulphate. Oil sands plants presently operate with large scale treatment of recycle process water and have a zero discharge policy due to the environment concerns. Consequently, the ionic content of the process water has been continuously increasing.

In order to validate the necessity of water pretreatment, thereby reducing the difficulty of dewatering from bitumen froth, it is important to determine the source and distribution of water present in bitumen froth. This study was set up to determine formation water distribution in the oil sands extraction process by using tracer technique. To accomplish the objective, Denver flotation cell was used to extract bitumen from oil sands ore. Poor, average and rich ores were tested. The composition of the ores and corresponding bitumen froth was analyzed by Dean-Stark method. More specific objectives of this study are:

- To analyze the concentration of tracer in the water of various streams collected during Denver Cell oil sands extraction process;
- To analyze the composition of oil sands ores and bitumen froth for different types of ores;
- To analyze the percent of fines in the ore and bitumen froth of different types of ores;
- To analyze the bitumen recovery of different types of ores;
- To analyze the percent of water at the specific level of diluted bitumen froth to make sure water settling status in bitumen froth for different types of ores; and
- To correlate the characteristics of ores, bitumen processability, bitumen froth quality and bitumen froth treatment performance with formation water distribution.

1.4 Organization of thesis

This thesis was organized as follows:

Chapter 1: History of oil sands industry and bitumen production methods were briefly introduced, followed by the objective of this study and the overview of this thesis.

Chapter 2: Fundamental knowledge of oil sands and bitumen extraction, including the composition and microstructure of the oil sands, was described. The mechanism of the emulsions stability was reviewed, and previous work on the use of tracer to analyze water distribution was briefly reviewed.

Chapter 3: Experimental equipment and procedures were described in detail.

Chapter 4: All the results and discussion were given.

Chapter 5: Conclusions were drawn based on previous analysis.

Chapter 6: Suggestions for future research in this field were provided.

Chapter 2: Literature Review

2.1 Oil sands compositions and characteristics

Oil sands primarily contain bitumen, water, sands and clays. The bitumen content in oil sands deposits varies from 0-16 wt.% by weight. Oil sands are classified usually by bitumen content: oil sands ores with bitumen content above 10 wt.% are considered as high-grade (rich) ore, an ore of bitumen content between 8-10 wt.% is considered as average-grade ore, and those with less than 8 wt.% are considered as low-grade (poor) ore. Although oil sands ores contain different grade of bitumen, the total content of bitumen and its formation water is fairly constant at around 16 wt.%. The rest of 84 wt.% is the mineral solids. Bitumen contains mainly carbon, hydrogen, sulphur, nitrogen, oxygen and metals present in organic structures. It is a mixture with extremely complex molecular structure. It is almost impossible to describe exact structures of all the components in bitumen. Some chemical elements of bitumen from the Athabasca oil sands are listed in Table 2-1 (Nelson and Gray, 2004).

Table 2-1: Typical composition of Athabasca bitumen

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

Classified by alkane solvent solubility, bitumen contains mainly two groups of organic components: asphaltenes and maltenes. Asphaltenes are the highest molecular weight component which is soluble in benzene but not in alkane solvent such as hexane. Athabasca bitumen contains 14-18 wt.% by weight of hexane-insoluble asphaltenes. The maltene fraction (alkane solvent soluble) can be further separated into following fractions: saturates, aromatics and resins.

The formation (connate) water content ranges from 0-9 wt.% by weight of oil sands ore. Normally, it is high in a poor ore, and low in a rich ore. The formation water contains different amount of inorganic and/or organic ions, such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2+}, HCO_3^- and/or –COOH. Table 2-2 shows composition and ion concentration in formation water of a rich oil sands ore and a poor oil sands ore from Syncrude Canada Ltd.

Table 2-2: Composition and ion concentration in formation water of a rich oil sands ore and a poor oil sands ore (Zhao, et al., 2009)

		Rich Ore	**Poor Ore**
Assays (wt.%)	Bitumen	14.3	6.1
	Water	3.4	7.0
	Solids	82.3	86.9
	Fines, <44 µm (of mineral solids)	12.8	43.0
Water Soluble Ions in "Formation Water" (mg/kg of ore)	Na^+	62.4	18.1
	K^+	5.2	19.8
	Ca^{2+}	0.3	32.0
	Mg^{2+}	0.1	18.4
	Cl^-	308.3	1.1
	SO_4^{2+}	13.5	118.4
	HCO_3^-	22.9	37.8
	pH	~7.0	~7.4

The mineral composition of the solids is over 90% quartz with minor amounts of potash, feldspar, chert and muscovite (Carrigy and Kramers, 1973; Boon, 1978; Masliyah 2004). Clay minerals, which are dominantly kaolinite, illite and a small amount of montmorillonite, only appear in the fines fraction. “Fines” is referred to the mineral solids that are smaller than 44 microns. A high-grade oil sands ore contains less fines, and a low-grade oil sands ore contains a larger amount of fines. Total solids analysis is given in Table 2-3.

Table 2-3: Mineral components of solids in a typical oil sands deposit (Helper and Smith, 1994)

Mineral	**wt.%**	**Mineral**	**wt.%**
Quartz	82	Kaolinite	4
K-feldspar	5	Illite	7
Calcite	Trace	Chlorite	1
Dolomite	Nil	Smectite	Trace
Siderite	Trace	Mixed layer clays	1
Pyrite	Nil	Anhydrite	Trace

2.2 Microstructure of oil sands

It is generally assumed that the hydrophilic nature of the sand grains is a key fact for the hot water process to be feasible (Camp 1976; Ball 1935; Cottrell 1963). It is hypothesized that a thin layer of water covers the entire surface of each sand grain. The presence of this water layer is the single most important characteristic and fortunate feature to make process of bitumen separation from oil sands easy and economically feasible. However, the existence of such a water film has not directly been verified experimentally.

In 1963, Cottrell was the first to propose a structural model for oil sands in terms of the mutual arrangement of solids, water and bitumen.

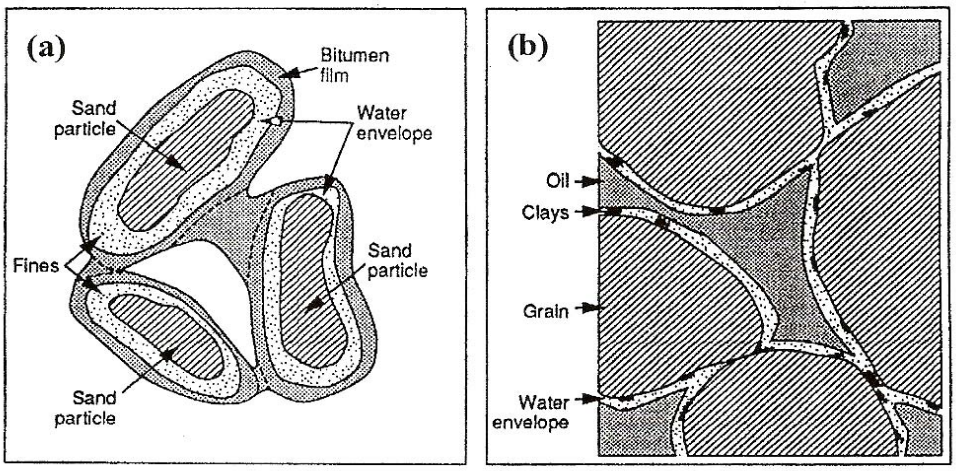

Figure 2-1: Sketch of model structure of oil sands proposed by (a) J. H. Cottrell (1963), and (b) G. D. Mossop (1980)

A schematic illusion of his model is shown in Figure 2-1(a). Cottrell assumed that the sand grains were surrounded by a water film of uniform thickness, while clay minerals were suspended in the water layer. This film of water was further encased by the bitumen, which filled the voids between the individual sand grains. Mossop updated the structure model in 1980. Figure 2-1(b) shows that the quartz grains were all in direct contact with each other, and they constituted a stable framework that remained virtually unchanged when the fluids were mobilized. The water film around the grains, only a few micrometers thick, formed a physically continuous sheath that prevented direct contact between bitumen and quartz. The bitumen phase was also continuous, linked from one pore to the next through a three-dimensional network of pore throats. Clay minerals were attached to the surface of sand grains, and it was unlikely that they protruded through the water envelop (Mossop, 1980). However, the above models have certain limitations: they assumed the thickness of the water film was uniform, and the models were only applicable to high-grade oil sands.

Takamura reported a refined model in 1982 which is shown in Figure 2-2.

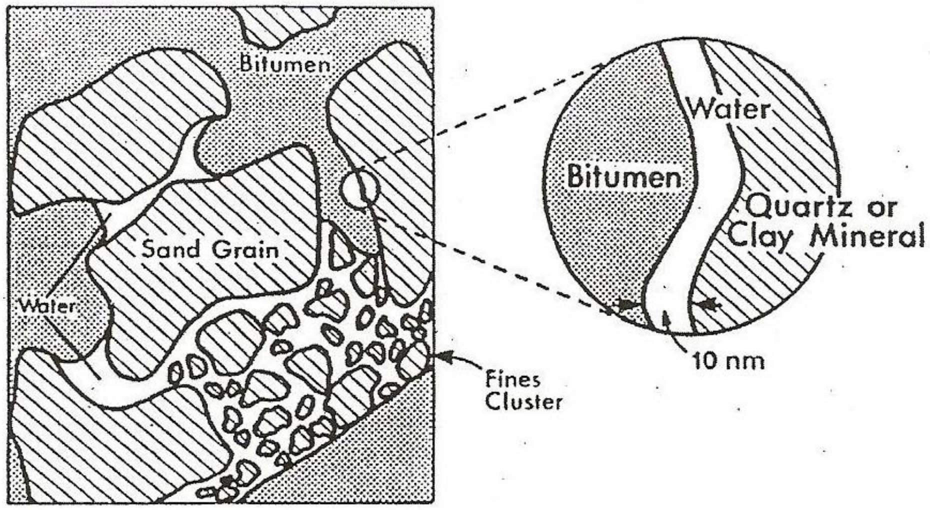

Figure 2-2: The refined structure model of Athabasca oil sands proposed by Takamura (1982).

In this model, the water in the oil sands appears in three forms: as pendular rings at grain-to-grain contact point; as a roughly 10 nm thick film which covers the sand surface; and as water retained in fines clusters. In the case of high grade oil sands, the pore space is filled with bitumen and water. The water occupies between 10-15% of the pore volume and forms pendular rings at the contact points between the sand grains. These pendular rings cover roughly 30% of the surface and the remaining 70% of the surface is covered by a thin film of water which is stable because of the double layer repulsive forces acting between the charged sands and the bitumen surfaces. In lower grade oil sands, clusters of fine particles (<44 μm) exist within the framework formed by coarse sand grains. These clusters of fine particles are saturated with water. Thus it provides an explanation that the amount of formation water in oil sands increases linearly with increasing fines content. The correlation between water content and fines content is illustrated in Figure 2-3.

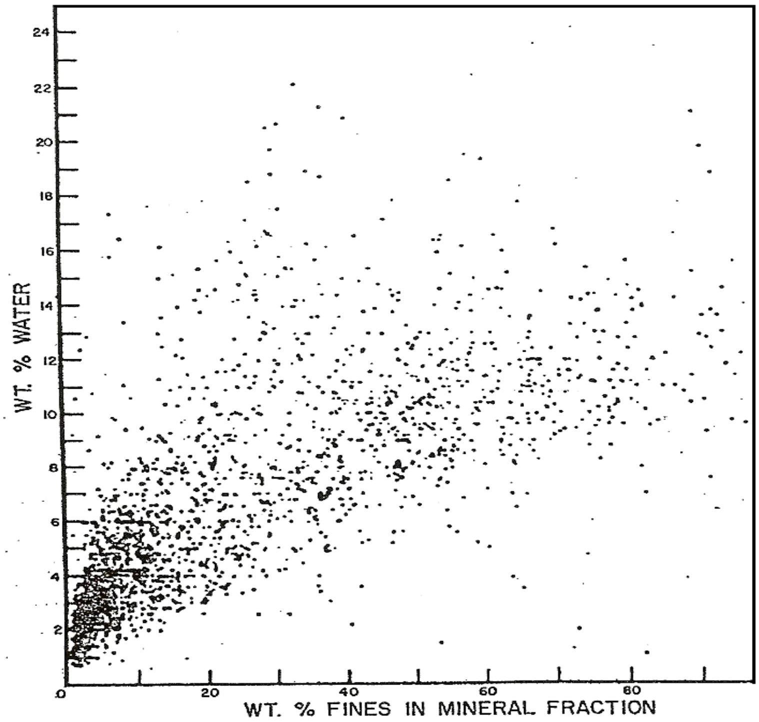

Figure 2-3: Correlation between water content and amount of fines in the solid fraction for different grade oil sands (Cameron Engineers, 1978)

2.3 Bitumen liberation

Takamura and Chow (1983) proposed a theoretical model for initiation of bitumen displacement from oil sands as shown in Figure 2-4. An oil sands aggregate is represented by two sand grains covered by a bitumen layer. When this aggregate is immersed in water, the bitumen migrates toward the grain-to-grain contact point and develops a toroidal shape [Figure 2-4(b)]. The interfacial area between the bitumen and water is smaller in this configuration, thus representing the thermodynamically more stable state. Sometimes minute bitumen flecks may be trapped in cavities or at sharp edges on the sand surface, thereby giving rise to the formation of small size droplets. When the bitumen starts accumulating at the grain-to-grain contact point, it also leads to the local thinning of the bitumen film, as schematically illustrated in Figure 2-4(c). Here the formation water layer is also shown. Electrostatic repulsion between the negatively charged bitumen-water and sand-water interfaces results in an increased disjoining pressure between the bitumen and solid phases. This disjoining pressure together with applied mechanical and thermal energy promotes the separation of the bitumen from the sand. When the bitumen film ruptures, this formation water is mixed with the aqueous phase into which the aggregate is immersed [Figure 2-4(d)]. The stability of the formation water film will be modified depending on the pH, and valence and concentration of electrolytes in the aqueous phase.

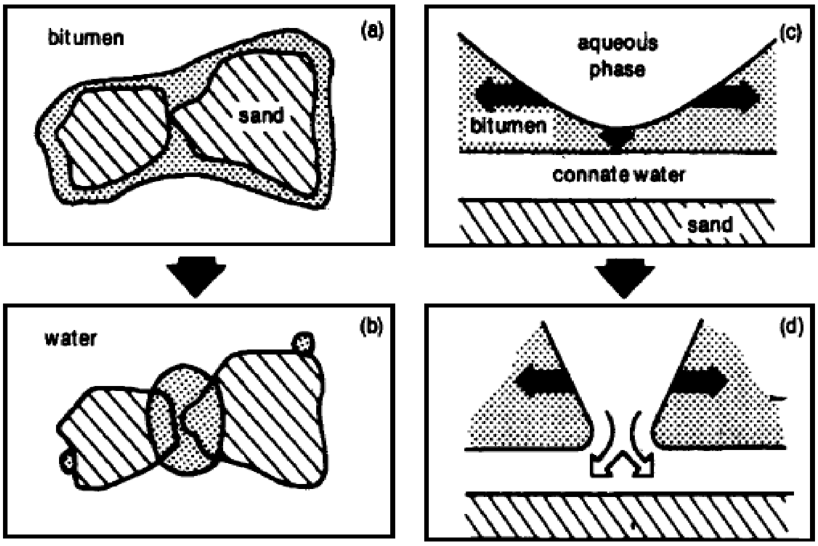

Figure 2-4: Schematic diagram showing the initiation of bitumen displacement (Takamura and Chow 1983)

2.4 Stability of water-in-oil (w/o) emulsions and mechanism of demulsification

The bitumen froth from the hot water extraction process consists of oil, water, solids and air. It has been found that a substantial amount of water in the bitumen froth is in the form of a water-in-oil emulsion. This emulsified water is difficult to separate from the bitumen froth.

2.4.1 Emulsion stability

According to Bancroft (1913), the stability of any emulsion is largely due to the nature of the formed interfacial film. The stability of this film is dependent on a number of factors, including the heavy organic components in the crude oil (e.g. asphaltenes, resins, saturates, and aromatics), solids (e.g. clays, scales, and corrosion product), temperature, droplet size and droplet-size distribution, pH, and composition of oil and brine. Adsorption–desorption kinetics, solubility of emulsifiers and their interfacial rheological properties are significant factors. Rheological properties are the main characteristics of the dynamic properties of a film. There are two rheological properties of interfacial films—interfacial shear and dilational viscoelasticity. It seems that dilational viscoelastic parameters are usually much larger than the shear ones. The difference can be of several magnitudes. Interfacial dilational viscoelasticity seems to play a significant role in emulsion stabilization (Bonfillon and Langevin, 1993).

According to four traditional separation methods, bitumen has been divided into asphaltenes, resins, aromatics and saturates, known as SARA. Among these, asphaltenes and resins have higher polarity and surface activity so that they will be adsorbed at an oil-water interface to form the interfacial film with considerable strength and stabilize emulsions. Therefore, research on emulsion stability has been mainly focused on asphaltenes. Many scholars believe that asphaltenes basically comprise of densified aromatic cycloparaffin as core, around which there link some cyclanes, aromatic hydrocarbon, and normal or isomeric alkane side chains with different length in cyclanes (Waller, 1989). Asphaltene molecule contains heteroatoms of S, N and O, and sometimes transition metals, such as Ni, V, Fe, etc. Resins and asphaltenes contain compounds of carbonyl and aromatic unit, which play a critical role in emulsion stabilization. Oxidation of interfacial materials has been found to increase both carbonyl content and emulsion stability. Among the interfacial material, the concentration of —C=O determines overall emulsion stability. However, the concentration of —OH is also found to be important. Both —C=O and —OH together promote asphaltenes molecule to form hydrogen bond, which surrounds droplets to avoid coalescing. The research of Mohammed et al. (1994) indicated that interfacial activity of asphaltenes is not very strong. Normally, oil-water interfacial tension in the presence of asphaltene is around 25-35 mN/m, but its ability to stabilize emulsions is strong. Natural surfactants, such as asphaltenes and naphthenic acids are found to adsorb at the oil-water interface and form interfacial film with elasticity. And the interfacial film formed from asphaltenes has sufficient strength to endure high pressure. In general, the higher, the asphaltenes content, the stronger, the film strength, and the more stable, the emulsions.

2.4.2 Mechanism of demulsification

Demulsification is to break an emulsion into oil and water phases. From a process point of view, the oil producer is interested in two aspects of demulsification: a fast rate at which this separation takes place and the low amount of water left in the crude oil after separation. The stability of an emulsion can be quantified as the time elapsed between its formation and its total collapse. Very concentrated emulsions (70% or more of the dispersed phase) are often in the form of polyhedral droplets separated by thin liquid films of the continuous phase (Figure 2-5).

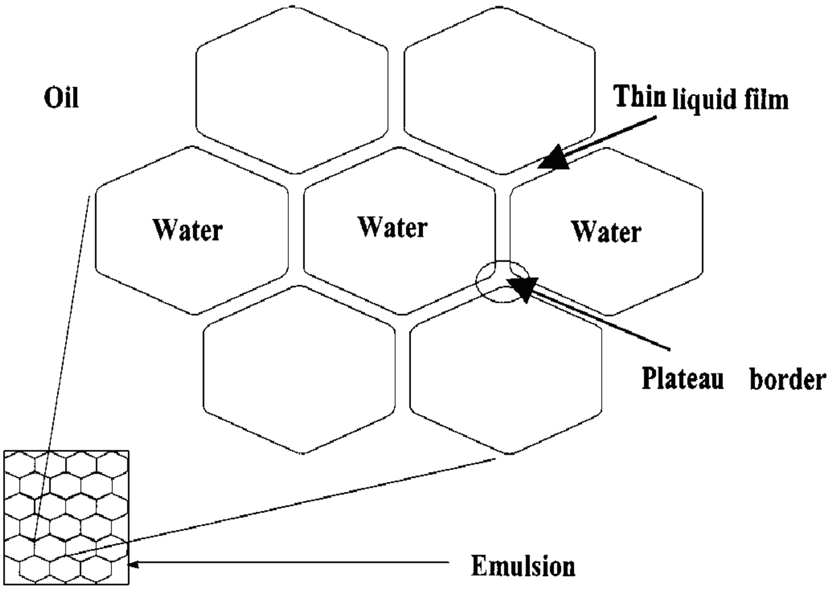

Figure 2-5: Polyhedral structure of concentrated water-in-oil emulsions (Socrates Acevedo, 2001)

Three adjacent liquid films meet at the Plateau border channels. The curvature at the Plateau border walls generates a pressure difference between the thin liquid film and the Plateau borders, causing liquid to flow out of the films into the Plateau border channels. Thus, the liquid films become thinner with time, and eventually they might collapse, promoting destabilization of emulsions. Therefore emulsion stability depends on the stability of the thin liquid films. The stability of the thin liquid films was first discussed in terms of a “disjoining pressure” by Derjaguin and Kussakov. The disjoining pressure is the pressure in the interior of the films, operating at right angles to the surface of the films, which opposes the approach and coalescence of two droplets in an emulsion. In other words, it is the force per unit area that opposes film drainage.

The purpose of demulsification is to destroy the interfacial film and make most water droplets to coalesce. In recent decades, researchers mainly focus on the mechanism of demulsification by following water droplet coalescence process and studying the influence of demulsifier on the rheological properties of interfacial film. It has become common sense that the demulsification includes three processes: droplet contact, liquid film thinning and coalescence. Demulsifiers are surface-active compounds. When added to an emulsion, they migrate to the oil-water interface. Since demulsifiers are of stronger interfacial activity than natural surfactant in bitumen, they will adsorb at the oil-water interface to partly displace natural emulsifiers adsorbed at the interface, forming a compound film with lower film strength. Eventually the rigid film will be broken to cause water droplets to coalesce, forming bigger drops which settle at a much faster rate. The coalescence leads to complete separation of oil and water phase, accomplishing demulsification. The factors that enhance or speed up emulsion breaking include: increasing temperature, solids removal, control of water chemistry and addition of chemical demulsifiers.

2.5 Previous study on tracing water

Sanford et al. (1992) carried out a series of experiments to study the formation of water-in-oil emulsions in the hot water extraction process. The experiments were conducted in a batch extraction unit (BEU) and a continuous pilot extraction test rig with Athabasca oil sands. Heavy water was used as slurry water or flood water in the BEU. The results showed that part of the slurry water was bound to the bitumen and formed emulsified water droplets in the primary froth. Microscopy studies showed that more droplets of smaller and more uniform sizes formed at high stirring speed. The maximum diameters increased from 7 to 23 μm when the stirring speeds decreased from 900 to 300 rpm. The maximum diameter of emulsified water droplets in the froth from the pilot scale extraction tests was about 18 μm. The BEU aeration procedure showed no effect on the emulsification process. The w/o emulsions in the primary froth from the hot water process were mostly caused by the process units in the slurrying step prior to the separation vessel. The w/o emulsions in bitumen froth were found to be extremely stable. The study of Sanford et al. mainly focused on when and which step the emulsified water formed, but it was not involved with formation water distribution, which is the focus of this study.

Chapter 3: Experimental Procedure

3.1 Analysis of oil sands ores

Five oil sands ore samples were used in this study. The composition of the ore samples was determined using standard Dean-Stark analysis procedures as described below.

3.1.1 Procedure for bitumen-water-solids analysis using Dean-Stark apparatus

Dean-Stark apparatus was invented by Dean and Stark in 1920 for determination of the water content in petroleum. It was used in this study to determine the composition of oil sands ores and bitumen froth quantitatively. Figure 3-1 shows a schematic diagram of a typical Dean-Stark apparatus.

A Dean-Stark apparatus consists of a burette-like vertical glass trap. The top of the cylindrical trap is connected to the bottom of a vertical glass tube which is a reflux condenser. The top of the trap has a side-arm sloping toward a reflux flask. A weighed filtering container, called thimble in which the sample is placed, is hung on the joint between the end of the side-arm and the reflux flask. About 200 ml toluene is placed in the flask prior to analysis. The flask with toluene is then heated up to boiling at 200 ^{o}C. The vapors containing toluene and water rise out of the flask into the condenser, and then into the distilling trap. Here, immiscible liquids are separated into two phases with toluene on top of water. When the top toluene layer reaches the level of the side-arm it flows back into the flask, while the bottom water phase is kept in the trap. During the refluxing, bitumen in the oil sands or froth is dissolved in hot toluene, which permeates the wall of thimble and drips in the flask. When the water level in the trap reaches the level of the side-arm, the water will flow back into the flask as well. It is important to drain the water from the trap as it accumulates. Reflux continues until the toluene dripping from the thimble becomes colorless and the level of the water in the trap is stable, usually lasting about 3 hours. At the end of refluxing, the collected water is carefully drained and weighed. The thimble is transferred into a glass jar and placed in the vacuum oven at 90 ^{o}C to dry over night. The dark organic liquid (bitumen in toluene solution) in the refluxing flask is allowed to cool down at room temperature and then transferred into a 250 ml flask. Additional toluene is added to the flask to 250 ml mark. After thorough mixing, 5 ml organic liquid is taken by a glass pipette and poured on a weighed filter paper evenly. After about 20 minutes in a well-ventilated fume hood, the toluene is completely evaporated, while the bitumen remains on the filter paper. The increase in the weight of the filter paper times by 50 is the total mass of bitumen in the given oil sands or bitumen froth originally placed in the thimble. The solid content is determined by the weight of dried thimble minus the original weight of empty thimble. The water content is determined by weighing the water collected. The bitumen-water-solids content is then obtained.

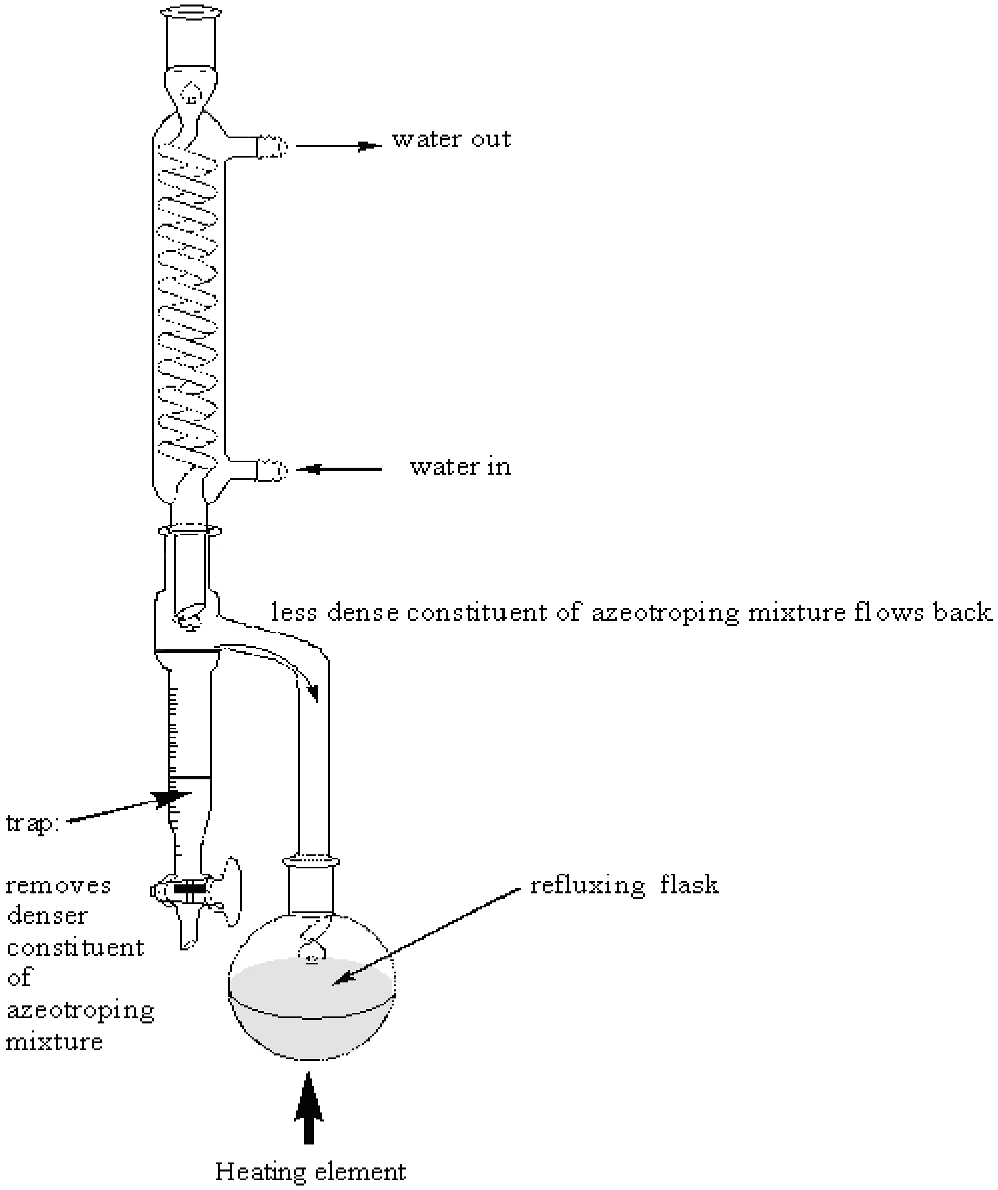

Figure 3-1: Schematic diagram of a Dean-Stark apparatus

3.1.2 Procedure for bitumen flotation tests

Bench-scale extraction unit, Denver Flotation Cell, was used to study ore processability and water distribution. The bitumen froth and tailings from Denver Flotation Cell tests were collected and analyzed using the above Dean-Stark method. Figure 3-2 shows a sketch of a typical Denver flotation cell.

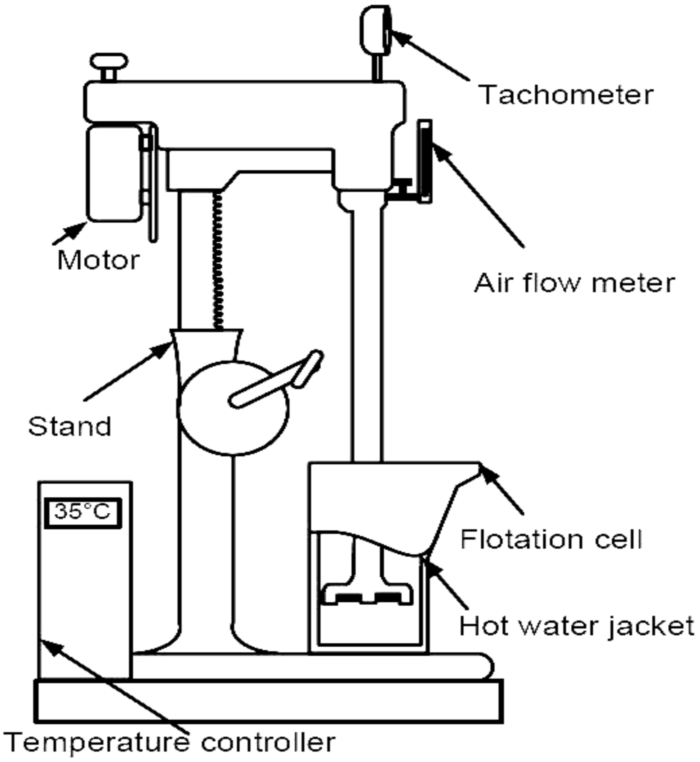

Figure 3-2: Schematic diagram of Denver flotation cell

The rotor in the center is fitted inside a solid stator composing a mixer. The bitumen is liberated from the solids under the shear force caused by rotating rotor at certain temperature. Air is introduced into the slurry through the central pipe along the stator, and broken into small bubbles within the area between stator and rotor. The air bubbles attach to bitumen droplets, decreasing the density of bitumen-air aggregates. The aerated bitumen droplets are then floated under buoyancy force to the top of the slurry in the flotation cell, forming bitumen froth.

The Denver cell flotation test was one of the most important steps of the study. A water jacket 1-liter flotation cell was connected to a thermal water bath, setting the temperature to 35 ^{o}C. After introducing 400 g of deionized water or processing water at 35 ^{o}C into the flotation cell, 130 g of defrosted oil sands ore was placed into the cell.

The agitation was then started at 1500 rpm to form bitumen slurry without aeration for 5 minutes. This step was referred to as oil sands conditioning. After conditioning, air flow at 150 ml/min was introduced into the flotation cell and aerated bitumen floated to the top of slurry, forming bitumen froth. For oil sands recovery study, bitumen froth was collected into four containers over desired time intervals of 3, 5, 10 and 15 minutes. For water distribution analysis of bitumen froth, the collected froth was placed in a 250 ml separation funnel.

Denver Cell flotation operational conditions were as follows:

- Medium: deionized water
- Temperature: 35 °C
- pH=8
- Aeration rate: 150 ml/min
- Stirring speed: 1500 rpm
- Conditioning time: 5 min
- Flotation time : 15 min

3.2 Heavy water experiments

3.2.1 Concept of experiments

Heavy water was first chosen as a tracer in this study. Normal water was replaced by heavy water as processing medium in flotation. The samples of water in bitumen froth and in tailings were collected. Since there was a density difference between the formation water and process heavy water, determining the density of water in bitumen froth and tailings would allow us to assess the source of water in bitumen froth and hence formation water distribution.

The density of water determined at 25 °C by density meter was as follows:

$$\rho_{H_2O} = 0.9973 \text{ g/cm}^3$$

$$\rho_{D_2O} = 1.1045 \text{ g/cm}^3$$

leading to a density difference of $\Delta\rho = 0.1072$ g/cm^3.

The density meter used in this study (DMA38, Anton Paar, Austria) could measure the density of water with a precision of one-thousandth, which was well above the density difference between the normal water and heavy water in the order of tens. It seemed that the density method was capable of discriminating the source of water in bitumen froth.

3.2.2 Materials

In this study, TS ore (bitumen 8.77 wt.%, water 9.37 wt.%, solid 81.86 wt.%) was first attempted. The reason to choose TS ore as first sample was that it contained the highest water content among the ores tested and was anticipated to provide the most reliable results. Heavy water (deuterium oxide, D_2O, 99%, density=1.1045 g/cm^3) was purchased from Cambridge Isotope Laboratories, Inc.

3.2.3 Experimental procedure

3.2.3.1 Density of formation water

Formation water contains high salinity, mainly Na^+; K^+; Ca^{2+}; Mg^{2+} etc. The high concentration of salt increases the density of formation water in comparison to pure water. It was therefore important to determine the density of formation water. The formation water was washed out from the oil sands ore by using heavy water. Since the density of D_2O had been already known, the density of formation water could be obtained from the density of the water mixture.

An accurate amount of heavy water was blended with TS ore. The solid-liquid mixture was shaken by a horizontal shaker (Reciprocal Shaker 6000, Ederbach, USA) at low speed for 60 minutes. After centrifuging the mixture at 15,000 rpm for 30 minutes, a part of water including formation water and added heavy water was separated from the solids. After collecting the released water, the density of water was measured, which allowed calculation of density of formation water using:

$$\rho_{Formation\,H_2O} = \frac{m_{Formation\,H_2O}}{V_{Formation\,H_2O}} = \frac{m_{Formation\,H_2O}}{\dfrac{m_{Added\,Water} + m_{Formation\,H_2O}}{\rho_{Mixture}} - \dfrac{m_{Added\,Water}}{\rho_{Added\,Water}}}$$

Results of three tests are summarized in Table 3-1.

Table 3-1: Density of formation water measurement for TS ore

	1	**2**	**3**
Ore (g)	20.449	23.933	21.886
Added Heavy Water (g)	5.871	11.086	10.627
Formation Water (g)=ore×9.37 %	1.916	2.243	2.051
Measured Density of Mixture (g/cm^3)	1.080	1.087	1.088
Calculated Density of Formation Water (g/cm^3)	1.011	1.008	1.009
Average Density of Formation Water (g/cm^3)	1.009±0.002		

Average value $\rho=1.009$ g/cm^3 was used as the density of formation water for future calculations.

3.2.3.2 Preparation of water samples

In a 1000 ml beaker, 65 g TS ore and 200 g heavy water were loaded. The initial pH of the mixture was measured to be 7.3 with no further chemical addition. To maintain whole procedure at a constant temperature, 300 ml water was added into the 1-litre Denver Flotation cell and the 1000 ml beaker was soaked in the water-containing flotation cell. Denver Cell flotation was carried on at the same conditions as mentioned in Section 3.1.2. The bitumen froth was completely skimmed off and diluted by 4 g naphtha, leading to a solvent-to-bitumen mass ratio of 0.7:1. After stirring, the diluted bitumen froth was loaded in a 250 ml separation funnel and allowed to settle for 24 hours at room temperature. The mixture was separated into four layers as shown in Figure 3-3.

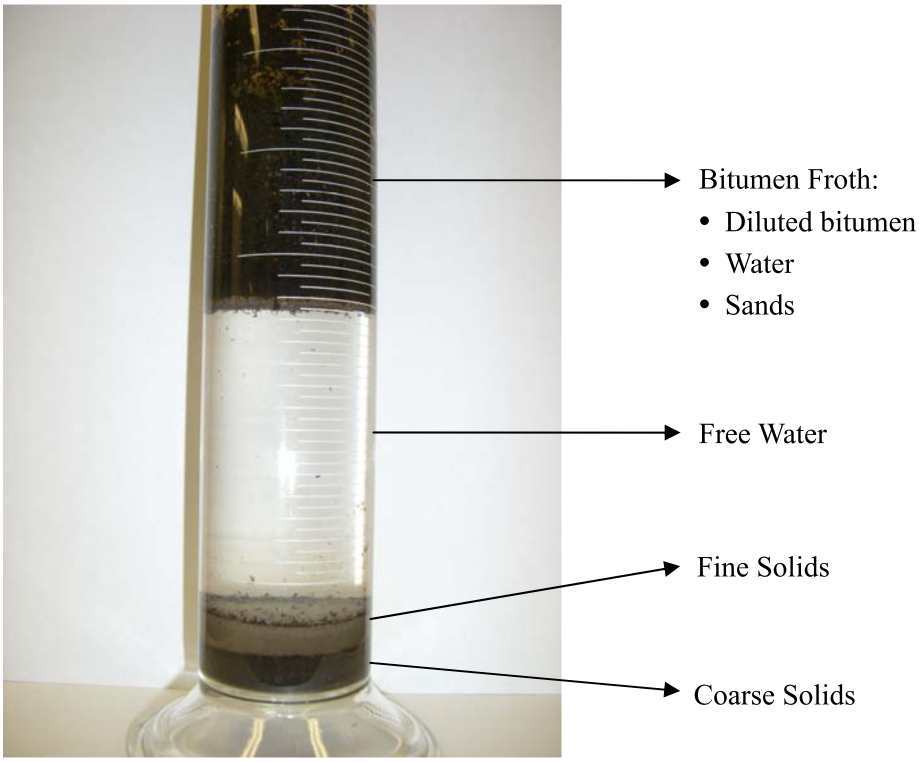

Figure 3-3: Four layers structure of diluted bitumen froth from TS ore after settling for 24 hours

The top oil phase was diluted bitumen. This oil phase contained solvent, bitumen, water and solids. Due to the addition of solvent, the average density of the bitumen-solvent mixture was lower than water. Diluted bitumen was therefore floating on the top. Beneath this top organic layer was an aqueous phase known as free water, which was released from the bitumen froth. At the bottom there were two layers of solids. In order to eliminate the error of collecting the free water and solids, they were drained off from the bottom outlet of the separation funnel by controlling the opening of the valve gently. The oil phase was collected and placed into a 30 ml centrifuge tube. After centrifuging for 30 minutes at 15,000 rpm, part of trapped water was separated out, as an aqueous layer as shown in Figure 3-4. The released water after centrifugation was defined in this study as emulsified water.

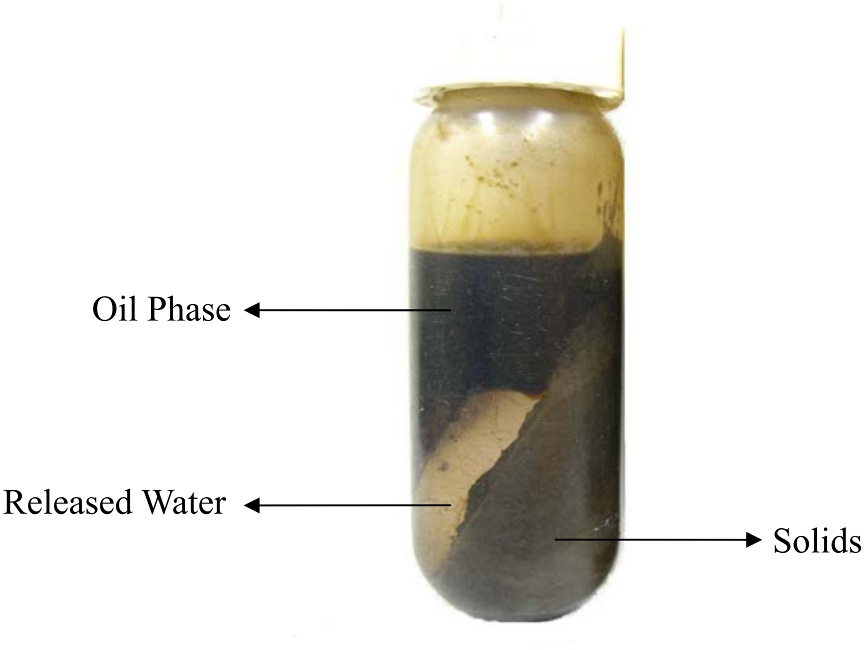

Figure 3-4: The diluted bitumen organic phase separated by high speed centrifugation

The liquid from aqueous layer was carefully collected by 2 ml glass pipette to minimize the trapping of oil droplet. The collected water was filtered using 25 mm syringe filter (pore diameter 0.22 µm, Fisher Scientific) to remove the clays and oil droplets. For density analysis, the tailings water and free water from the same set of experiment were also filtered using the same method.

3.3 Electrical conductivity measurement

The electrical conductivity of water samples from oil sands extraction was measured. Although it could not give a quantitative conclusion, a qualitative analysis could be achieved. Electric conductivity is a measure of a material to conduct an electric current. It is the inverse of electrical resistivity, and has the SI units of siemens per metre ($S \cdot m^{-1}$). The formation water is known to contain higher salinity which leads to higher conductivity. The conductivity of water samples from Section 3.2.3.2, including processing water, emulsified water, free water and tailings water, was measured by Zeta Potential Analyzer (BrookHaven Instruments Corporation, USA).

3.4 Chemical tracer experiments

3.4.1 Concept of experiments

At the early stage of this study, heavy water experiments and conductivity measurements were found to be not sufficiently sensitive to distinguish distribution of formation water. An alternative chemical tracer method was developed. In this method, a chemical element which was not present in the oil sands ore was added to the deionized water that was used as the processing water for bitumen extraction. Once an oil sands ore was extracted by such tracer-containing processing water, the determination of tracer element concentration in various water samples would allow the distribution of formation water in various water samples to be assessed. A lower concentration of tracer element in a water sample would indicate a higher concentration of formation water in that sample. Tracer analysis could provide a material balance calculation and hence more quantitative conclusion. Identifying a chemical tracer which did not interfere with extraction, did not adsorb on oil sands components during extraction, and could be easily and accurately measured, was the key for the entire project.

3.4.2 Chemical tracer selection and solution preparation

The criteria taken into consideration to select the tracer are as follows:

1. It should be completely soluble in water but highly insoluble in organic phase;
2. Accurate analysis is possible even at low concentrations;
3. It should not be present in the original oil sands ore;
4. Introduction of such tracer should not cause chemical reaction with the bitumen and has no effect on bitumen extraction; and
5. It should not adsorb on oil sands components in oil sands extraction process.

Cobalt (Co) was selected as tracer in this study. The main reason of choosing cobalt as tracer is that oil sands ore does not contain any detectable amount of Co. Secondary, cobalt can be easily and accurately analyzed by Atomic-Absorption Spectroscopy (AAS). Accurate measurements can be achieved to less than 1 ppm of metal ion concentration. Other metals, such as Ca, Mg and Al can be precisely detected by AAS analysis as well, but the presence of such metals at appreciable concentration in oil sands ore disqualifies them as candidates.

To avoid adsorption of Co^{2+} on various components of oil sands, chelating of Co^{2+} with EDTA to form a high soluble, stable complex was applied. In preparation of 40 ppm Co tracer solution, a stoichiometric amount of Co (0.5 g $CoCl_2$ dehydrated at 100 ^{o}C, blue powder) and EDTA (1.43 g EDTA disodium salt) was placed in a 500 ml flask. Deionized water was added to the 500 ml mark. The 40 ppm pink Co in EDTA complex solution was used after dilution by 10 times with water. The Co-EDTA is highly soluble in water, and more stable than other metal-EDTA complexes as shown by corresponding high complexation constant in Table 3-2.

Table 3-2: EDTA complex stability constant

Ions	**Co^{2+}**	**Al^{3+}**	**Fe^{2+}**	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}**
logK	16.31	16.11	14.32	10.69	8.70	1.66

In Table 3-2, K refers to EDTA complexation stability constant, given by $K = \frac{\left[Co(EDTA)^{2-}\right]}{\left[Co^{2+}\right]\left[EDTA\right]}$. With a value of Log K=16.31, it means that the concentration of Co-EDTA is 10^{16} time higher than the product of concentration of Co ions and EDTA molecules in solution. A high value of K means less dissociation of Co-EDTA complex in water, namely the Co-EDTA complex is very stable in water.

3.4.3 Chemical tracer feasibility experiments

3.4.3.1 Bitumen recovery

As mentioned in the previous section, the introduction of a chemical tracer should not affect bitumen extraction. Two sets of oil sands extraction experiments were carried out at the same conditions in order to validate that the Co-EDTA addition did not affect bitumen recovery. The only difference between these two tests was that the processing water in one test contained 40 ppm Co in EDTA complex form, but not in the other test.

The test was conducted using 200 g TS ore in 600 g processing water. The initial pH value of the mixture for both tests was adjusted to be 8 by 0.1 mol/L NaOH solution. The flotation tests were conducted in standard Denver Flotation Cell as described in Section 3.1.2. During flotation, the bitumen froth was collected at exact time intervals of 3, 5 and 10 minutes after air addition. The bitumen recovery results of the two tests are shown in Figure 3-5.

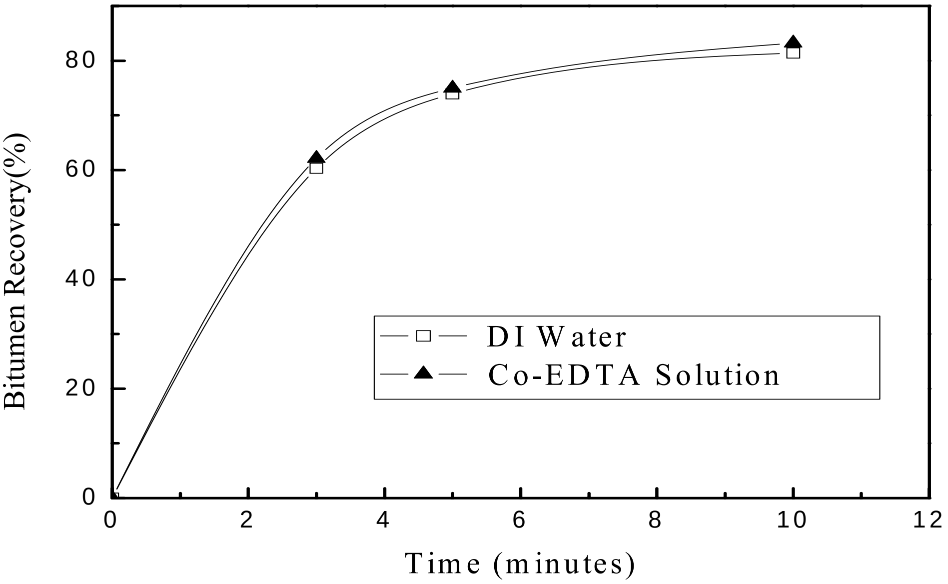

Figure 3-5: Bitumen recovery obtained from two procedures at the same extraction condition

It is evident from Figure 3-5 that two bitumen recovery curves almost superimpose on each other. This finding indicates that introducing cobalt-based chemical tracer in the form of Co-EDTA complex does not alter bitumen recovery characteristics.

3.4.3.2 Loss of tracer in extraction of weathered oil sands ore

Whether a tracer is applicable or not is highly depended on whether it disappears or not from processing water. Because of the complex nature of oil sands composition, many situations may lead to loss of tracer from water by adsorption. Extracting bitumen from a weathered ore which contains minute quantity of formation water with tracer-contained water was carried out to test the loss of the tracer. Without the effect of formation water, and comparing the concentration of cobalt in processing water with that in the water after extraction test, whether the tracer disappears or not can be determined. If the concentrations of cobalt are the same in the processing water and tailings water after extraction, it indicates that the adsorption does not take place. On the contrary, if the concentrations of cobalt are different, Co^{2+} can be possibly trapped by solids because of cation exchange or Co-EDTA molecule may be adsorbed on the surfaces.

In this test, 200 g TS ore was dried in vacuum oven at 80 °C for 48 hours. A small amount (60 g) of this weathered ore was analyzed by Dean-Stark to determine water content remained in the weathered ore. The results in Table 3-3 show that almost all original formation water was removed during weathering. The remaining weathered ore was then extracted with 38.6 ppm Co-EDTA solution at pH=8 by Denver Flotation Cell.

Table 3-3: Effect of weathering on ore composition

	Bitumen	**Water**	**Solids**
Original Ore (wt.%)	8.77	9.37	81.86
Weathered Ore (wt.%)	9.98	0.27	89.75

The water samples were collected using the same procedures as described in Section 3.2.3.2. The concentration of cobalt is given in Table 3-4.

Table 3-4: Results of weathered ore extraction experiments

Water	**Processing**	**Emulsified**	**Free**	**Tailings**
Co (ppm)	38.6	38.2	38.4	38.5

The experimental results using the weathered ore clearly show that, after the extraction, the concentrations of cobalt in various water samples are comparable to the concentration in the processing water, and distributed evenly in whole system. This finding indicates that Co-EDTA is a good tracer for our targeting objective of analyzing formation water distribution.

3.4.4 Cobalt tracer experiments

3.4.4.1 Bitumen froth settling

Water plays a critical role in oil sands extraction. Bitumen is liberated and floated in water. In bitumen froth, water exists in two forms: stable emulsified water and free water. The emulsified water is protected by a thin layer of strong surface activity substance (such as asphaltenes) and fine solids, hence it is extremely difficult to be removed from the bitumen froth. The free water, on the other hand, can be release from the bitumen froth by a mild external force. By applying a sufficient external force (such as centrifuge) or adding a demulsifier, the emulsified water can be transformed into free water. In this study, emulsified water was given top consideration. Existence of free water would cause large experimental errors. Removal of this free water prior to water analysis would greatly improve the accuracy of analysis.

The bitumen froth from TS ore extraction was diluted by naphtha to a naphtha to bitumen mass ratio of 0.7. The diluted froth was loaded in a graduated cylinder, and allowed to settle for 48 hours. During this period, the level of oil-water interface was recorded at certain time intervals. The interface level as a function of settling time is shown in Figure 3-6.

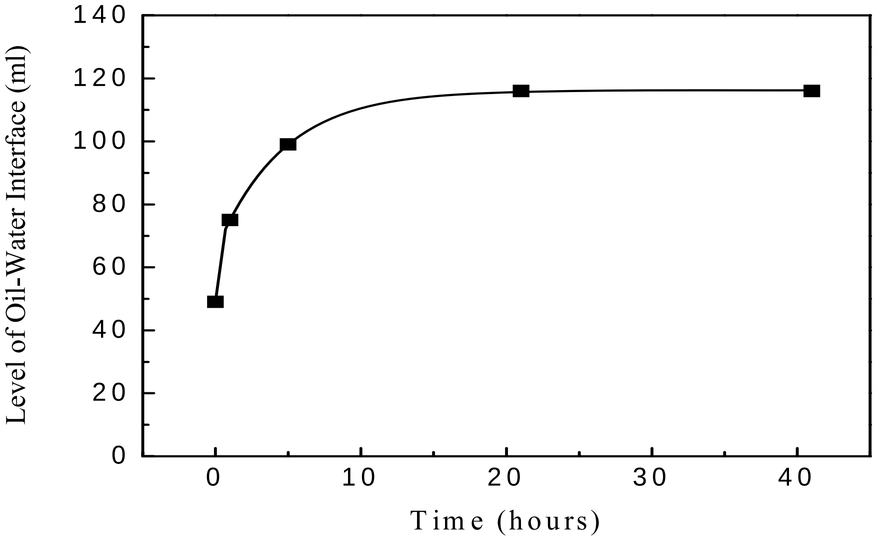

Figure 3-6: Variation in the level of released free water with time

Figure 3-6 shows that the free water separated out continuously with time, leading to an increase of the interface level. The quantity of released water shows minimal changes after 24 hours, indicating completion of free water drainage. A 24-hour settling to drain the free water was used in all further experiments.

3.4.4.2 Co-EDTA tracer experiments and mass balance calculations

In this study, several ores with different characteristics were tested to determine the effect of ore characteristics on formation water distribution. In this section, TS ore is used as an example to illustrate the experimental procedures and mass balance calculations. Prior to extraction test, about 130 g TS ore and 400 g prepared Co-EDTA processing water were weighed accurately and blended in a 1000 ml beaker. Since it is necessary to collect all tailings at the end of the experiment, a 1000 ml beaker was used instead of the Denver Flotation Cell. After adding 300 g water into Denver Cell to keep the temperature at 35 ^{o}C by a constant heating system, the 1000 ml beaker was fixed in the flotation cell, immersing in the water of constant temperature.

Denver Cell flotation was run with 5 minutes conditioning and 3 minutes aeration. With continuing aeration, bitumen froth was collected for 15 minutes into a 250 ml separation funnel. The bitumen froth was diluted with 6.5 g naphtha to obtain a solvent to bitumen mass ratio of 0.7:1, which was based on the condition of the industrial froth treatment operation. The mass of bitumen in froth is determined based on mass of ore (130 g) times known bitumen content of ore (8.77 wt.%) times known bitumen recovery (81%). The diluted froth was stirred gently by a glass rod to homogenize the mixture.

In order to calculate the mass balance of cobalt, water mass balance should be considered first. The strategy was to collect water in all the streams of an extraction test. Since the collected water normally contained solids, the weight loss method after completely evaporating the collected water, was used. In this case, the difference between the weight of the total collected sample (container, solids and water) and the dried sample (container plus solids) was the net weight of water.

In this test, the mass of tailings water, free water and emulsified water was calculated respectively. For tailings water after the oil sands extraction by Denver Flotation Cell, the tailings sample was allowed to settle for half hour. About 20 ml muddy tailings was transferred into a 30 ml Teflon centrifuge tube, leaving the rest of tailings in the beaker. At this stage, some water with sands was still adhering to the wall of rotator and stator. The best way to collect it was to wrap the stator with paper of high water absorption capacity and turn on the rotor. With the high speed rotation of rotor, water and sands were thrown off and absorbed by the paper. All the paper used to wrap the stator was put into the tailings-containing beaker. The beaker containing tailings and wet paper was weighed and placed in a vacuum drying oven at 80 ^{o}C for 48 hours. The other part of tailings in centrifuge tube was sent to centrifuge at 15,000 rpm. Under high speed centrifugation, clear water was separated from solids. About 10 ml "clean" water was collected and weighed. This water was analyzed by AAS. The rest in the centrifuge tube was weighed and sent to vacuum drying oven as well. Table 3-5 summarizes the experimental data.

Table 3-5: Mass balance calculation of tailings water for TS ore

Beaker + Tailings		**Tailings Sample (g)**	**Tube + Tailings**	
Wet (g)	Dry (g)	10.17	Wet (g)	Dry (g)
839.49	508.32		36.39	26.83
Difference (g)				
331.17		10.17	9.56	
Net Weight of Tailings Water (g)				
350.90				

To release the free water, diluted bitumen froth was allowed to settle for 24 hours.

This was based on the result from Section 3.4.4.1, which showed a complete release of free water after 24 hours of settling. Free water was drained out and analyzed using the same procedure as for tailings water. Table 3-6 shows the experimental data for TS ore.

Table 3-6: Mass balance calculation of free water for TS ore

Beaker + Free water		**Free water Sample (g)**	**Tube + Free water**	
Wet (g)	Dry (g)	10.05	Wet (g)	Dry (g)
70.38	46.36		28.31	23.43
Difference (g)				
24.02		10.05	4.88	
Net Weight of Free Water (g)				
38.95				

For the emulsified water in the diluted bitumen, since there were three phases (water, oil, solids) in the bitumen froth, the situation was more complicated. It was possible that the light component of bitumen might evaporate during drying. If this was true, the mass loss of organics would be included in the water, leading to an inevitable calculation error. To exclude this error, a froth drying experiment was conducted. The bitumen froth was collected by Denver Cell flotation from TS ore. This bitumen froth was settled for 24 hours without solvent addition and split into two parts. One part was analyzed for composition by Dean-Stark; the other part was weighed and placed in vacuum drying oven at 80 °C. The data obtained are given in Table 3-7.

Table 3-7: Results of bitumen froth drying experiment for TS ore (all in grams)

Bitumen Froth for Dean-Stark Analysis			**Bitumen Froth for Drying**	
70			70	
Bitumen	**Water**	**Solids**	**Before Drying**	**After Drying**
27.2	26.2	16.6	474.95	448.9
Absolute Difference			**Difference**	
26.2 - 26.05 = 0.15			26.05	

The data in Table 3-7 indicate that the difference between the mass of water by Dean Stark analysis and drying experiment was 0.57%. This difference included loss of organics by evaporation and experimental error. It was established that the loss of organics was sufficiently small that it could be neglected for further calculations.

About 25 ml diluted bitumen obtained from the test described at the beginning of this section for mass balance calculation was transferred into a 30 ml centrifuge tube. After centrifuging at 15,000 rpm, the froth was separated into three layers as shown in Figure 3-4. The clear water (5 ml) from the middle layer was taken, weighed and analyzed by AAS. The remaining diluted bitumen was weighed and placed in vacuum drying oven at 80 ^{o}C for 48 hours. Since the naphtha added as diluent would be completely evaporated, the known mass of naphtha should be deducted from the total mass loss. The data obtained are given in Table 3-8.

Table 3-8: Mass balance calculation of water in the bitumen froth for TS ore

Funnel + Froth		**Water Sample (g)**	**Tube + Froth**	
Wet (g)	Dry (g)	5.62	Wet (g)	Dry (g)
78.56	63.81		40.07	34.50
Difference (g)				
14.75		5.62	5.57	
Naphtha (g)		**Net Weight of Emulsified Water (g)**		
6.50		19.44		

At this point in the mass balance experiments, the mass of water in each stream of the system was obtained, and the cobalt concentrations in various water samples were determined. The total water balance in the system is shown in Figure 3-7.

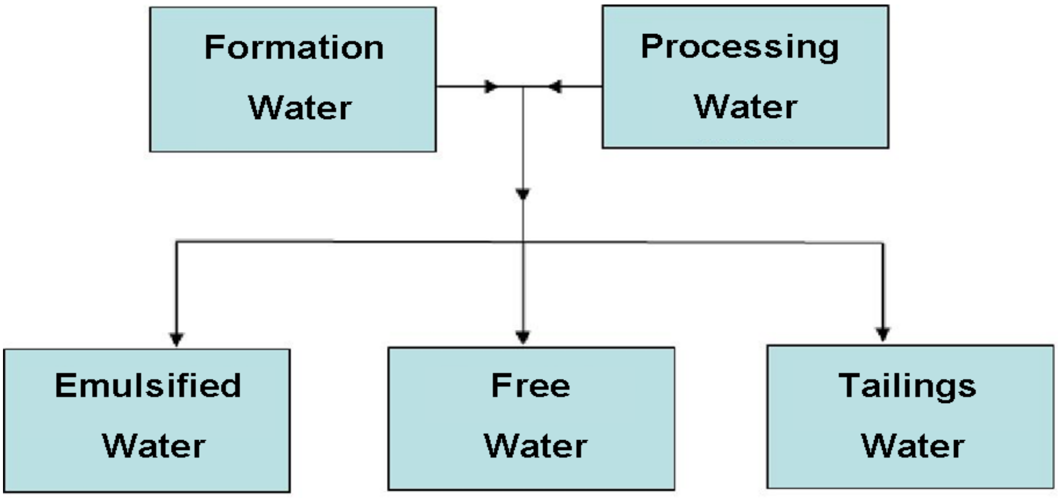

Figure 3-7: Water distributions in oil sands extraction test

The data for water mass balance calculation are given in Table 3-9.

Table 3-9: Water mass balance calculation (all in grams)

<table>
<tr><th colspan="2">Formation Water</th><th colspan="2">Processing Water</th><th>Total Water</th></tr>
<tr><td colspan="2">12.18</td><td colspan="2">400.04</td><td>412.22</td></tr>
<tr><td>Emulsified Water</td><td colspan="2">Free Water</td><td>Tailings Water</td><td>Total Water</td></tr>
<tr><td>19.44</td><td colspan="2">38.95</td><td>350.90</td><td>409.29</td></tr>
<tr><td>Absolute Error</td><td colspan="2">2.93</td><td>Relative Error</td><td>0.71%</td></tr>
</table>

Based on water mass balance, mass balance of cobalt can be obtained as shown in Table 3-10.

Table 3-10: Cobalt mass balance calculation for a sample test

<table>
<tr><th>Feed</th><th>Formation Water</th><th colspan="2">Processing Water</th><th colspan="2">Total</th></tr>
<tr><td>Water</td><td>12.18 g</td><td colspan="2">400.04 g</td><td colspan="2">412.22 g</td></tr>
<tr><td>Co</td><td>0 ppm</td><td colspan="2">36.6 ppm</td><td colspan="2">14641.5×10^{-6} g</td></tr>
<tr><td>Product</td><td>Emulsified Water</td><td>Free Water</td><td colspan="2">Tailings Water</td><td>Total</td></tr>
<tr><td>Water</td><td>19.44 g</td><td>38.95 g</td><td colspan="2">350.90 g</td><td>409.29 g</td></tr>
<tr><td>Co</td><td>34.6 ppm</td><td>35.2 ppm</td><td colspan="2">35.4 ppm</td><td>14465.5×10^{-6}g</td></tr>
<tr><td colspan="2">Absolute Error of Co</td><td>176×10^{-6} g</td><td colspan="2">Relative Error</td><td>1.2 %</td></tr>
</table>

The results of cobalt mass balance experiment show an overall 1.2 % cobalt loss during the oil sands extraction test. The results here are consistent with those obtained with laboratory weathered oil sands ore, described in Table 3-4 where Co-EDTA complex balance was established. Considering the complex procedures of extraction, sampling and analysis, this level of material balance was considered acceptable for further chemical tracer experiments.

Chapter 4: Results and Discussion

4.1 Composition analysis of oil sands ores by Dean-Stark method

The Dean-Stark method described in Section 3.1.1 was applied to five oil sands ore samples and the results are given in Table 4-1.

Table 4-1: Descriptions and compositions of different ores

Ore Type	Source	Description	Bitumen	Water	Sands	Fines
			(wt.%)			
POSYN	Syncrude	Poor Ore	5.91	7.43	86.66	43.0
TS	Syncrude	Transition Ore	8.77	9.37	81.86	33.0
SYN704	Syncrude	Average Ore	9.39	5.38	85.23	25.5
Vince A2	Aurora	Rich Ore	11.27	3.13	85.60	12.6
AL711	Shell	Rich Ore	13.21	2.73	84.06	13.4

It is clear that the five oil sands ores used in this study cover a wide range of characteristics in the content of bitumen, water and solids.

4.2 Bitumen recovery of oil sands ore samples

Bitumen recovery from five diverse grade ores (Denver-Cell test, deionized water as processing water, 35 ^{o}C, pH=8, 15 minutes bitumen froth collection) is given in Table 4-2.

Table 4-2: Bitumen recovery and bitumen froth quality of five ores

Ore Type	**POSYN**	**TS**	**SYN704**	**Vince A2**	**AL711**
Bitumen Recovery (%)	77	81	75	76	66
Bitumen/Solids (wt./wt.)	0.24	1.5	1.17	0.76	1.28

A wide range of processability in the context of bitumen recovery from 66% to 81% is evident.

4.3 Results of heavy water tests

In this study, all the density data were measured by Anton Paar density meter (DMA38). The density of the heavy water which functioned as processing water was 1.1045 g/cm^3. Density of the formation water measured in Section 3.2.3.1, $\rho=1.009$ g/cm^3 was used for calculation.

The materials used in heavy water test included TS ore (bitumen 8.77 wt.%, water 9.37 wt.%, solid 81.86 wt.%) and heavy water (deuterium oxide, D_2O, 99%). The pH values of processing medium (D_2O) adjusted by NaOH D_2O solution and density of water samples collected using procedures described in Section 3.2.3.2 are given in Table 4-3. The density of well-mixed water, i.e. the density of water calculated by assuming a complete mixing of the processing medium with formation water is also given in Table 4-3. The measured density of various water samples is compared with the density of well-mixed water in Figure 4-1.

Table 4-3: Density of water samples

pH	7.22	9.09	10.16	11.04
Density of Emulsified Water (g/cm^3)	1.1015	1.1012	1.1015	1.1013
Density of Tailings Water (g/cm^3)	1.1018	1.1010	1.1014	1.1015
Density of Well-Mixed (g/cm^3)	1.1013			

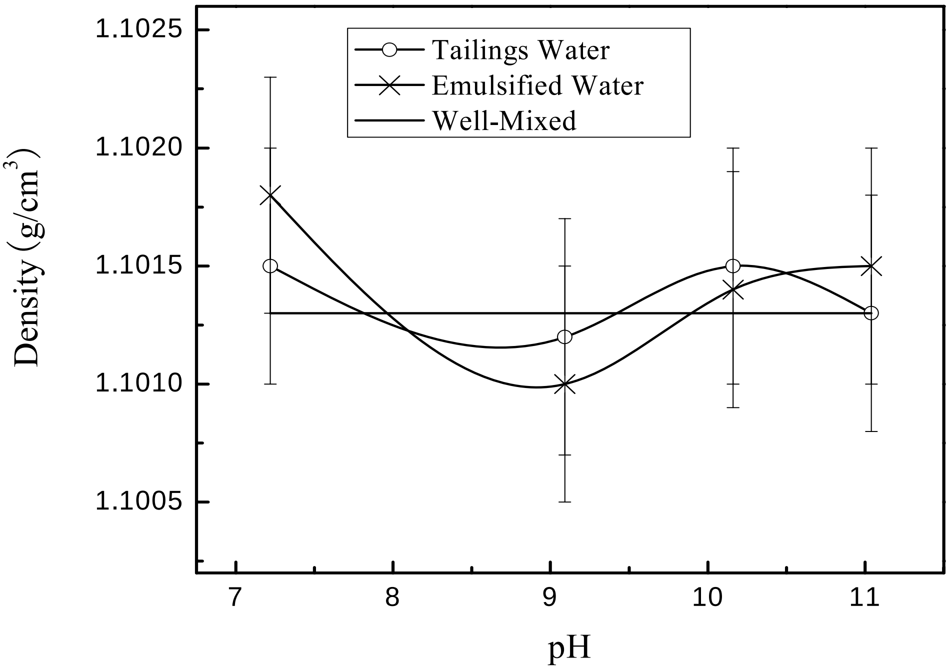

Figure 4-1: Density of water samples

The results in Figure 4-1 show large variations in the measured density of emulsified water and tailings water. There was no clear trend. Considering the error bars of the experiments, the difference in density between emulsified water and tailings water was considered within the experimental error. It was evident that this method did not provide a clear conclusion on formation water distribution in bitumen froth and tailings.

4.4 Results of electrical conductivity measurements

TS ore was used in electrical conductivity experiments. The initial pH of the mixture was measured to be 7.3 with no further chemical addition. The conductivity values of various water streams obtained at 25 °C are shown in Figure 4-2.

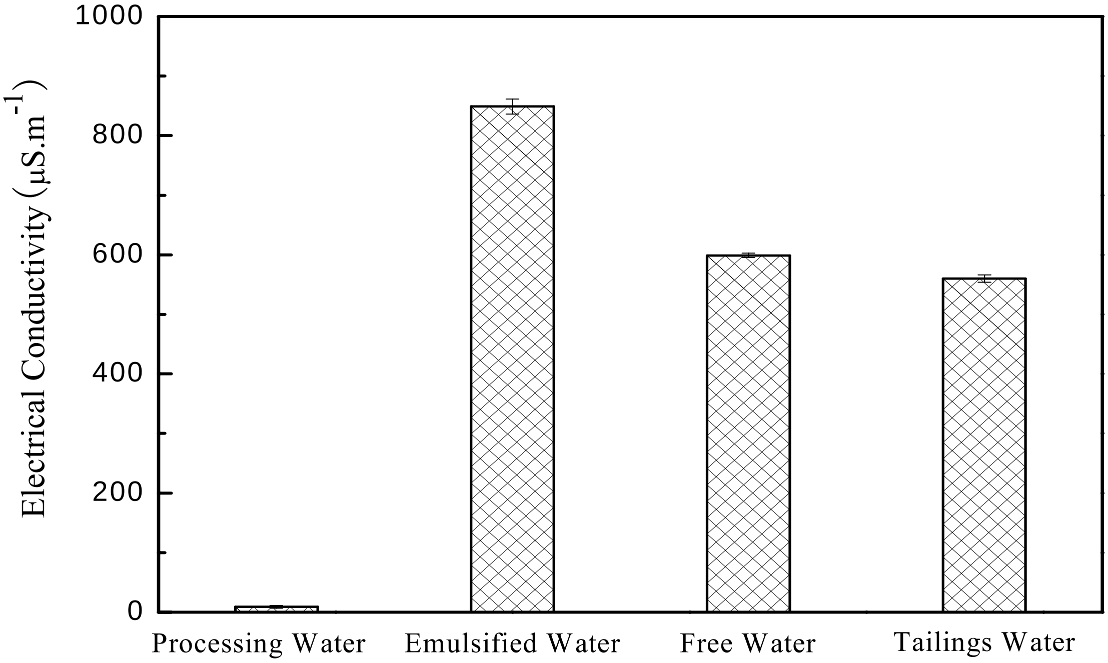

Figure 4-2: Conductivity of water samples

The conductivity of emulsified water was found to be 40% higher than that of free water and tailings water. This finding suggested that the amount of salts in the emulsified water was higher than that in the other water samples. It appeared that the formation water of high salinity was more likely emulsified and stayed in the bitumen froth. It is important to note that the conductivity of tailing water was much higher than the processing water. Although the salts could come from two sources: one in the original formation water; and the other released from solids during flotation, there is no reason why more ions are distributed in the emulsified water. The results in Figure 4-2 suggested that the ions released from the solids were more likely evenly distributed in free and tailings water. It could therefore be deducted that high salinity formation water was preferentially partitioned in the bitumen froth, most likely in the form of emulsified water. Due to the complication of ions released from solids, this method could not provide a quantitative analysis on formation water distribution.

4.5 Results of chemical tracer experiments

The purpose of the chemical tracer experiment developed in this study was to investigate the distribution of formation water in oil sands hot water extraction test. Chemical tracer added in the processing water played a significant role in identifying formation water distribution which was an important role in emulsion stabilization encountered in froth treatment.

4.5.1 Cobalt concentration

In this section TS ore will be analyzed as an example, further analysis and comparison of more ores will be discussed in the next section. The concentrations of cobalt in all water samples derived from Section 3.4.4.2 were analyzed by AAS, as shown in Table 4-4 (numbers 1, 2, 3 indicate three sets of repeat experiments).

Table 4-4: Cobalt concentration in different water samples collected during bitumen extraction using TS ores

	Co (ppm)				
	Test 1	**Test 2**	**Test 3**	**Average**	**Standard Deviation**
Processing Water	36.6	38.1	37.5	37.4	0.8
Formation Water	0	0	0	0	0
Emulsified Water	34.6	35.5	34.7	34.9	0.5
Free Water	35.2	36.8	36.2	36.1	0.8
Tailings Water	35.4	37.0	36.3	36.2	0.8
Well-Mixed	35.5	37.0	36.4	36.3	0.8

The conditions of these experiments were 130 g of TS ore containing 12.18 g formation water, 400 g of processing water.

In Table 4-4, the concentration in the well-mixed water is the cobalt concentration of water when the processing water is assumed to be completely mixed with the formation water, i.e. the amount of Co in the processing water divided by total water, including formation water plus processing water. According to the data in Table 4-4, the cobalt concentration in the emulsified water is lower than in the well-mixed water. This finding indicates that formation water without cobalt accounts for larger proportion in the emulsified water, as compared to the well-mixed situation. The ratio of formation water and processing water in emulsified water, free water and tailings water will be given in the next section.

4.5.2 Water distribution calculations

An assumption is made that the emulsified water comes from two sources: formation water and processing water. The nomenclature for water distribution calculation is given as follows:

m_f: mass of water in emulsified water arising from formation water.

m_p: mass of water in emulsified water arising from processing water.

C_f: concentration of cobalt in original formation water (0 ppm).

C_p: concentration of cobalt in the added processing water.

C_e: concentration of cobalt in the emulsified water.

C_w: concentration of cobalt in a well-mixed case.

Based on the principle of mass conservation applied to cobalt, the equation to calculate the fraction of formation and processing water in the emulsified water of the bitumen froth is

$$m_f \cdot C_f + m_p \cdot C_p = (m_f + m_p) \cdot C_e$$

Since $C_f = 0$, above equation can be simplified to

$$\frac{m_p}{m_f + m_p} = \frac{C_e}{C_p} \quad ; \qquad \frac{m_f}{m_f + m_p} = 1 - \frac{C_e}{C_p}$$

In above equations, $m_f + m_p$ represents the mass of emulsified water in the bitumen froth. Thus the processing water fraction of emulsified water can be expressed as C_e / C_p; the formation water proportion of emulsified water can be expressed as $1 - C_e / C_p$.

The calculated results of percent of formation water and processing water in the emulsified water are shown in Table 4-5.

Table 4-5: Percent of formation water and processing water in emulsified water for TS ore

	Co (ppm)			
	Test 1	***Test 2***	***Test 3***	**Average**
Processing Water (C_p)	36.6	38.1	37.5	37.4
Formation Water (C_f)	0	0	0	0
Emulsified Water (C_e)	34.6	35.5	34.7	34.9
Well-Mixed (C_w)	35.5	37.0	36.4	36.3
	Percent Water in Emulsified Water (%)			
	Test 1	***Test 2***	***Test 3***	**Average**
Arising from Processing Water $\left(C_e / C_p\right) \times 100\%$	94.54	93.18	92.53	93.42
Arising from Formation Water $(1-\frac{C_e}{C_p}) \times 100\%$	5.46	6.82	7.47	6.58
Well-Mixed (Processing Water) $\left(C_w / C_p\right) \times 100\%$	96.99	97.11	97.07	97.06
Well-Mixed (Formation Water) $(1-\frac{C_w}{C_p}) \times 100\%$	3.01	2.89	2.93	2.94

The above calculations are not only suitable for emulsified water, but also applicable for free water and tailings water. The calculated results of free water and tailings water are listed in Table A-4 in Appendix. The mass of formation water and processing water in every stream can be obtained based on the data in Table A-4. The detailed results are listed in Table A-5.

The data in Table A-5 do not seem to have any trend. However, close analysis of the data provides some insights on formation water distribution as shown by the results in Table 4-6.

Table 4-6: Distribution of water (%) for TS ore

	Emulsified Water	**Free Water**	**Tailings Water**
Total Water Distribution	3.83	12.85	83.32
Formation Water Distribution	7.61	13.88	78.51
Processing Water Distribution	3.70	12.82	83.48

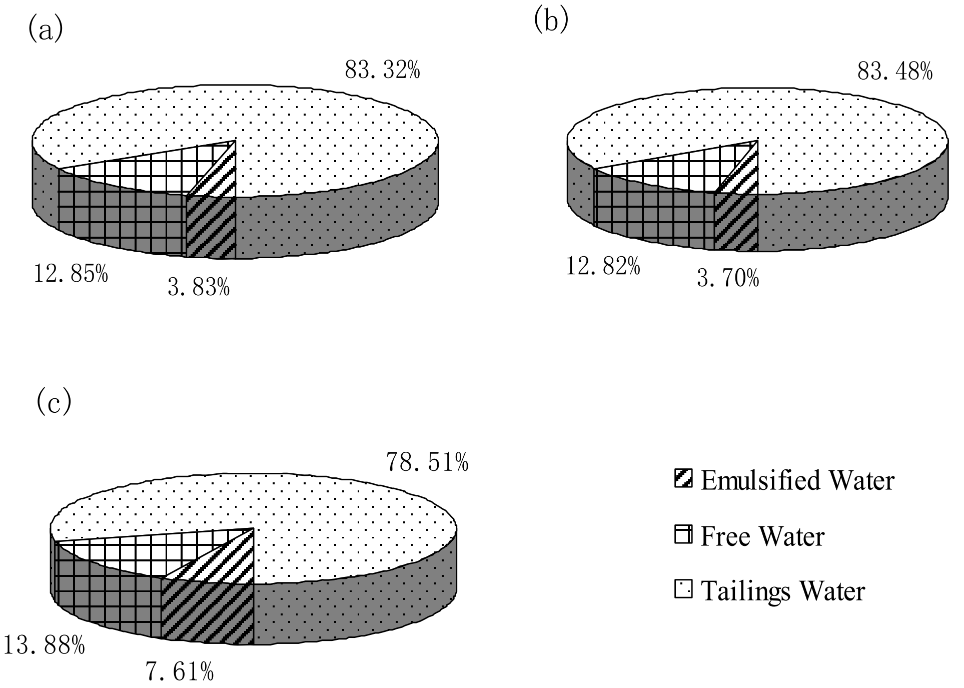

Figure 4-3: (a) Total water distribution; (b) Processing water distribution; and (c) Formation water distribution.

The results in Figure 4-3 indicate that, distribution of processing water in free water and tailings water resembled distribution of total water due to its dominance in the whole system when compared with the amount of formation water. For the formation water, a part of it appeared to be isolated in oil phase from contacting processing water during flotation and floated with bitumen to the top of slurry as bitumen froth, leading to a higher distribution of formation water (lower cobalt concentration) as the emulsified water than that of the processing water as the emulsified water in the bitumen froth.

4.5.3 Chemical tracer experiments for other ores

In the above section, a single ore (TS) was analyzed as an example to find the source of emulsified water. It is well known that the ores from different mining locations have specific characteristics. Only after analyzing several ores, the correlation between ore characteristics and formation water distribution can be found. Five diverse grade ores were used in the tracer experiments. The compositions of these ores determined by Dean-Stark analysis are given in Table 4-1 and bitumen recoveries determined by Denver Cell Flotation are given in Table 4-2. The feed and water used in oil sands extraction tests for five ores are given in Table A-1. The results of chemical tracer experiments are given in Table A-2 to Table A-11 and presented in the form of pie chart in Figure A-1 to Figure A-5 in appendix.

The correlation between percent formation water in emulsified water and percent formation water in oil sands ore is shown in Figure 4-4.

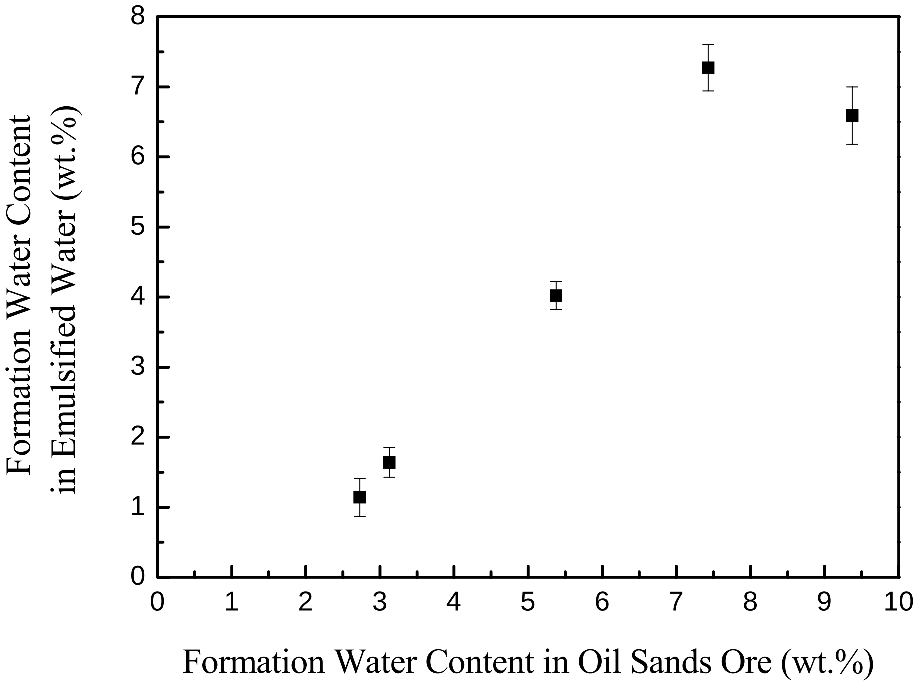

Figure 4-4: Correlation between percent formation water in emulsified water and percent formation water in oil sands ore

The correlation in Figure 4-4 between formation water content in emulsified water and that in oil sands ore is less evident. A maximum formation water content in emulsified water is shown at 7.5% formation water of oil sands ore. Among these tested oil sands ores, it is possible that a higher original percent formation water in an ore leads to a higher percent formation water in emulsified water. Without a base line for comparison, an ore with higher percent formation water in emulsified water can not account for more preferential distribution of formation water in bitumen froth.

To better determine the preferential distribution of formation water in emulsified water, the percentage of formation water in emulsified water was normalized by the percentage of formation water in even distribution case. This ratio is referred to as the selectivity index of formation water distribution. A larger selectivity index value would indicate a more preferential distribution of formation water in emulsified water. After linking the selectivity index of formation water with oil sands ore characteristics, the factors which affect the formation water distribution in oil sands extraction process can be found. The percent formation water in the emulsified water and selectivity index for five tested ores are given in Table 4-7. It is interesting to note that the formation water was preferentially distributed in the bitumen froth during extraction for all five ores, as indicated by the selectivity index above 1.

Table 4-7: Percent formation water in emulsified water and selectivity index of formation water

Ore Type	**POSYN**	**TS**	**SYN704**	**Vince A2**	**AL 711**
(A) Percent Formation Water in Emulsified Water (measured) (%)	7.27	6.58	4.02	1.64	1.14
(B) Percent Formation Water in Emulsified Water (well-mixed)(%)	2.36	2.96	1.70	1.01	0.88
Selectivity Index (A/B)	3.08	2.22	2.36	1.62	1.29

4.5.3.1 Correlation between formation water selectivity index and characteristics of oil sands ores

In order to determine the factors that affected the formation water distribution in the oil sands extraction process, the links between the characteristics of oil sands ores and formation water selectivity index are investigated.

The percent bitumen and percent formation water in the five ores (Table 4-1) determined by Dean-Stark method were correlated with the formation water selectivity index in Figure 4-5 and 4-6.

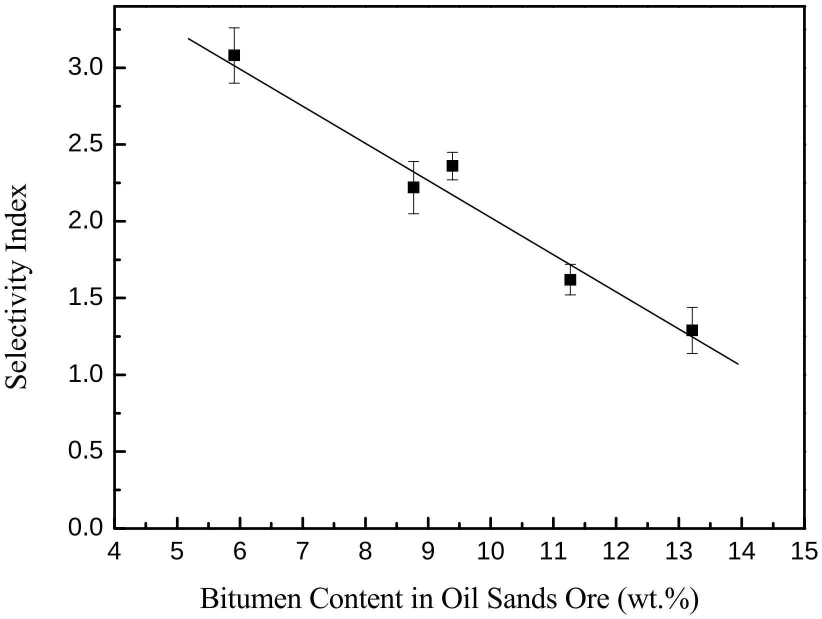

Figure 4-5: Correlation between percent bitumen in oil sands ore and formation water selectivity index

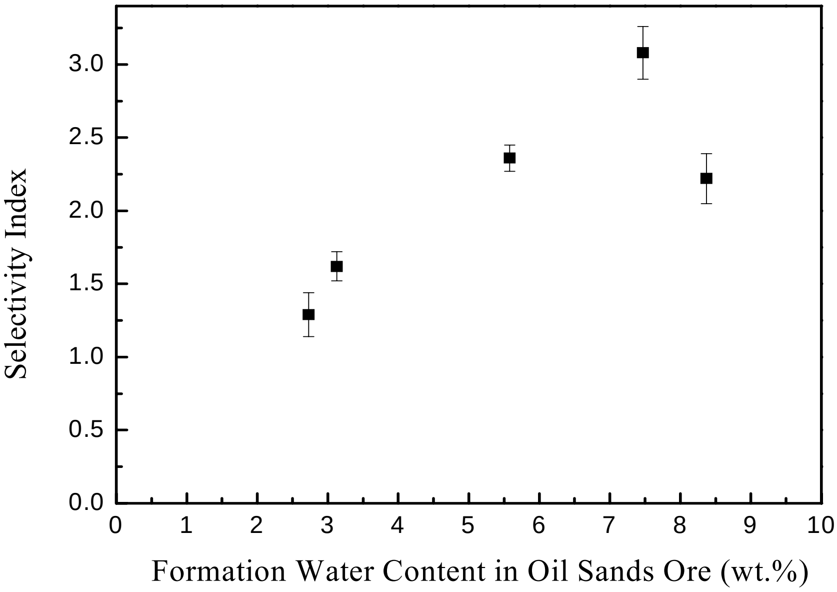

Figure 4-6: Correlation between percent formation water in oil sands ore and formation water selectivity index

Figure 4-5 shows that the selectivity index of formation water decreases with increasing ore grade, suggesting that the formation water tends to distribute more evenly for rich ores than poor ores. The correlation between selectivity index and formation water content in the ore is less evident, showing a maximum in selectivity index at 7.5% formation water. It appears that the original formation water content in the ore plays a less critical role in determining formation water distribution in emulsified water.

4.5.3.2 Correlation between selectivity index of formation water and percent fines

The stability of any emulsion is largely due to the nature of the interfacial films. In addition to temperature, droplet size and droplet-size distributions, the stability of this film also depends on a number of factors, including the heavy organic components in the crude oil (e.g. asphaltenes, resins, saturates, and aromatics), solid (e.g. clays, fines), pH, and brine composition. Fines (less than 44 microns in size) are considered as a factor that affects the formation water distribution.

In order to evaluate the effect of fines in the bitumen froth on formation water distribution, the bitumen froth from all five ores were processed at the same conditions as described below. The naphtha as diluent was added into the bitumen froth obtained from Denver Cell flotation test, to 70% mass of bitumen. The diluted bitumen froth was allowed to settle for 24 hours. After draining all free water, the diluted bitumen froth was separated into solids, bitumen and water by Dean-Stark method. The solids were placed in a vacuum drying oven at 80 ^{o}C overnight. The percentage of fines was determined in this study by wet-sieving the dried solids.

Lumps of dried solids sample were first gently broken apart by mortar and weighed. The solids were then placed in a 44 μm sieve for wet sieving in a water bath. The surface of clays at this stage was found to be hydrophobic. Direct wet sieving was difficult to perform in such case as all solids were floating on the surface of water. Pre-wetting the solids by acetone helped to disperse the solids and hence facilitate wet-sieving. The wet sieving continued till no more solids were washed into the water bath. After wet sieving, all the solids retained on the sieve were larger than 44 μm in size. The oversize fraction of solids was dried and weighed to calculate the percentage of fines. Percent fines of solids in the original oil sands ores and corresponding diluted bitumen froth are given in Table 4-8.

Table 4-8: Percent fines in oil sands ores and corresponding diluted bitumen froth (percent fines of total solids wt.%)

Ore Type	**POSYN**	**TS**	**SYN704**	**Vince A2**	**AL 711**
Percent Fines in Oil Sands Ore (%)	43	33	25	14	13
Percent Fines in Diluted Bitumen Froth (%)	62	50	46	36	24
Difference (%)	31	34	45	61	46

The correlation between percent fines in oil sands ore and corresponding diluted bitumen froth and formation water selectivity index is shown in Figure 4-7 and 4-8.

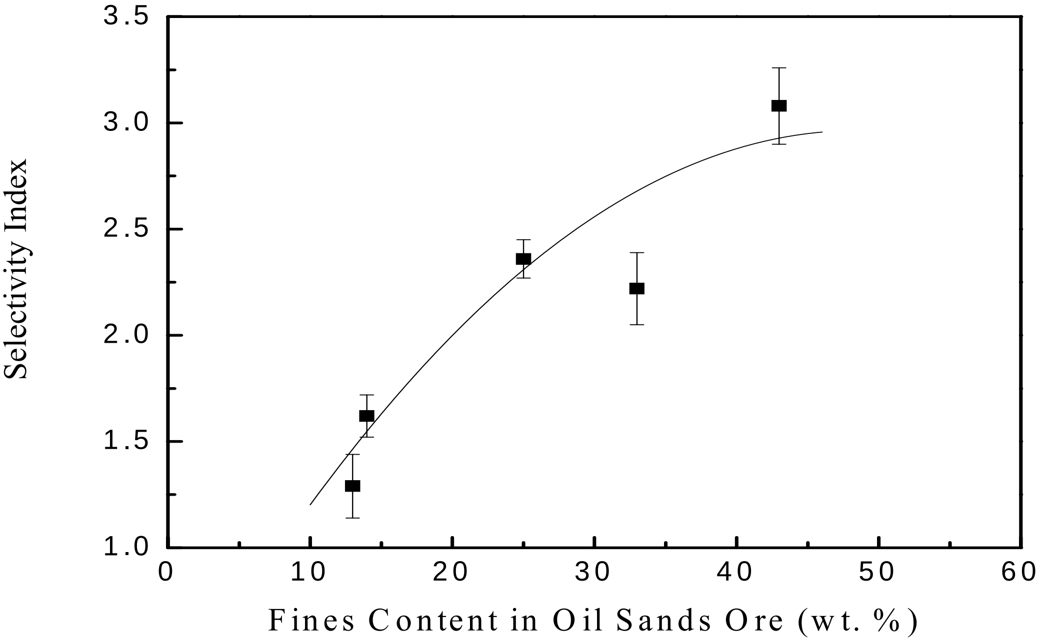

Figure 4-7: Correlation between formation water selectivity index and percent fines in oil sands ore

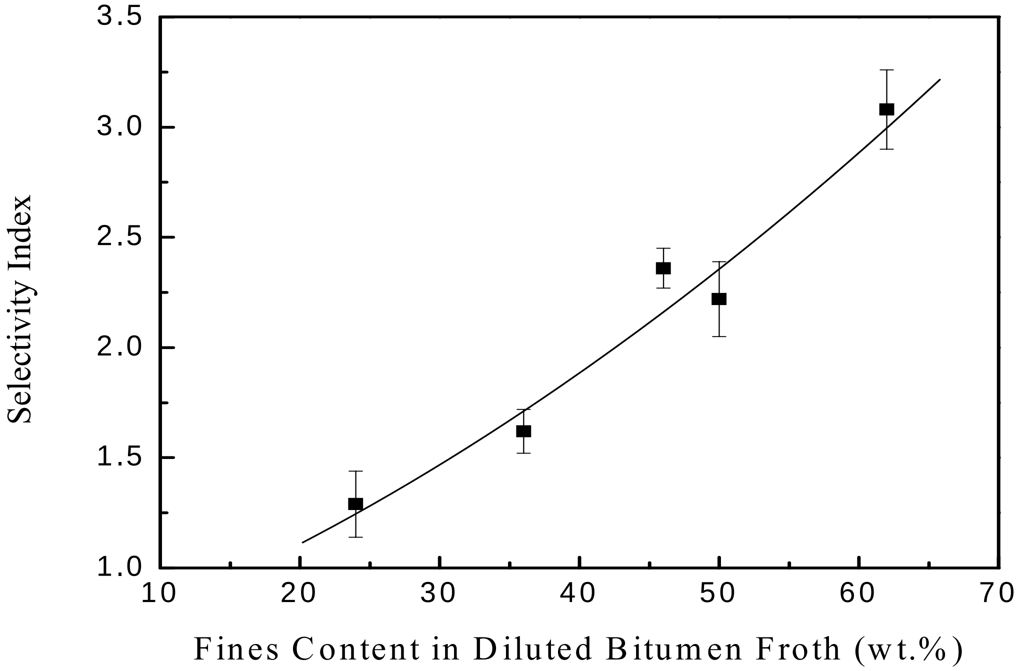

Figure 4-8: Correlation between formation water selectivity index and percent fines in diluted bitumen froth

It is evident from Figure 4-7 and 4-8 that formation water in emulsified water appears to follow the percent fines, regardless in oil sands ore or diluted bitumen froth, increasing selectivity index with increasing fines content either in the ore or in bitumen froth.

4.5.3.3 Correlation between formation water selectivity index and bitumen recovery

There are two important stages affecting bitumen recovery: liberation and aeration. Aeration is affected by the surface characteristics of air, bitumen and sands, as well as processing water chemistry, rather than the formation water itself. For liberation, it is possible that processing water intermingles with the formation water at this step. How intimately they contact each other is directly reflected in the distribution of formation water, i.e. by selectivity index. The bitumen recovery of the five ores as a function of formation water selectivity index is shown in Figure 4-9.

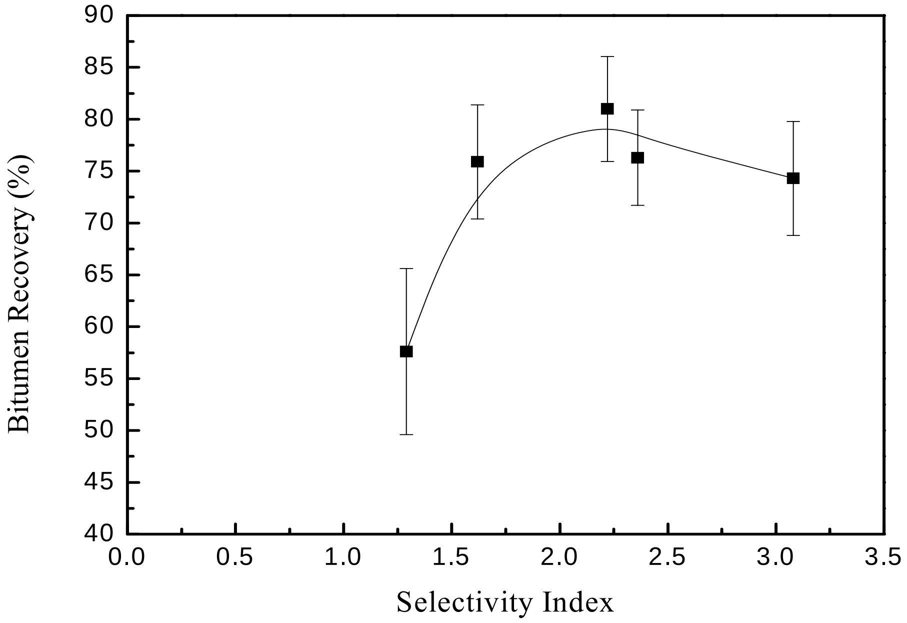

Figure 4-9: Bitumen recovery as a function of formation water selectivity index

Although highly scattered, the results in Figure 4-9 show a positive correlation:

bitumen recovery increases with increasing formation water selectivity index. It appears that more formation water encapsulated in bitumen without contacting processing water leads to high bitumen recovery.

4.5.3.4 Correlation between formation water selectivity index and bitumen froth quality

The bitumen froth was obtained from aforementioned five ores by Denver Flotation Cell tests, and allowed to settle for 24 hours without naphtha addition. After the removal of free water and associated solids, the bitumen froth was analyzed by Dean-Stark method. The results are given in Table 4-9

Table 4-9: Froth composition of five oil sands ores

Ore Type	**Bitumen***	**Water**	**Solids**	**Bitumen/Water**	**Bitumen/Solids**
	(wt.%)			**(wt./wt.)**	
POSYN	9	54	37	0.17	0.24
TS	36	40	24	0.90	1.50
SYN704	35	35	30	1.0	1.17
Vince A2	32	26	42	1.23	0.76
AL 711	45	20	35	2.25	1.28

** Feed bitumen content*

The results in Table 4-9 show that the bitumen froth from rich ore contains less water than that from poor ore. The selectivity index of formation water is compared with bitumen-to-water mass ratio in bitumen froth in Figure 4-10.

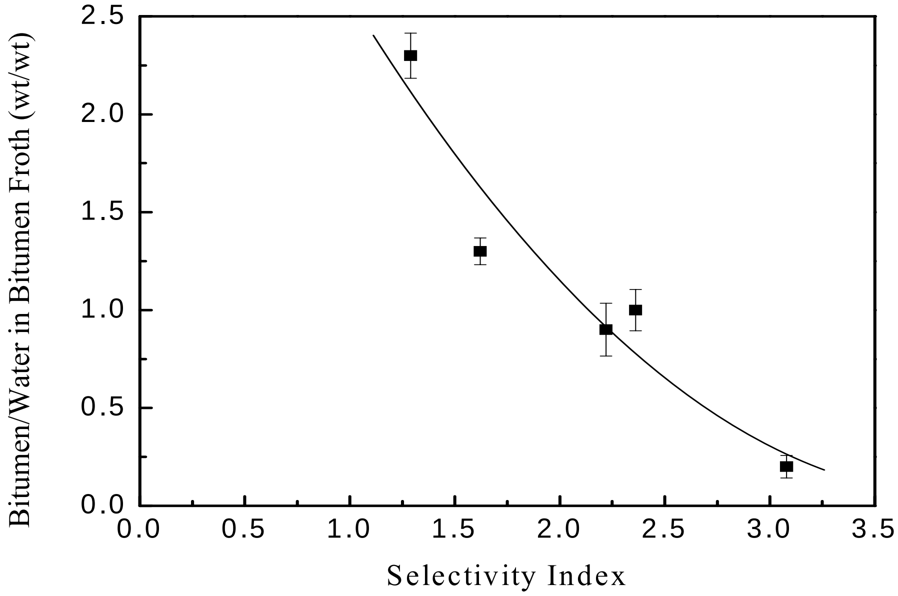

Figure 4-10: Bitumen-to-water mass ratio in bitumen froth as a function of formation water selectivity index

The comparison in Figure 4-10 suggests that ores with large selectivity index of formation water lead to a poor bitumen froth quality, i.e., low bitumen to water mass ratio. It appears that preferential distribution of formation water in bitumen froth is detrimental to the bitumen froth quality. Complete mixing of formation water with processing water indicated by a selectivity index close to unity leads to the highest bitumen froth quality.

The selectivity index of formation water is compared with bitumen-to-solids mass ratio in bitumen froth in Figure 4-11.

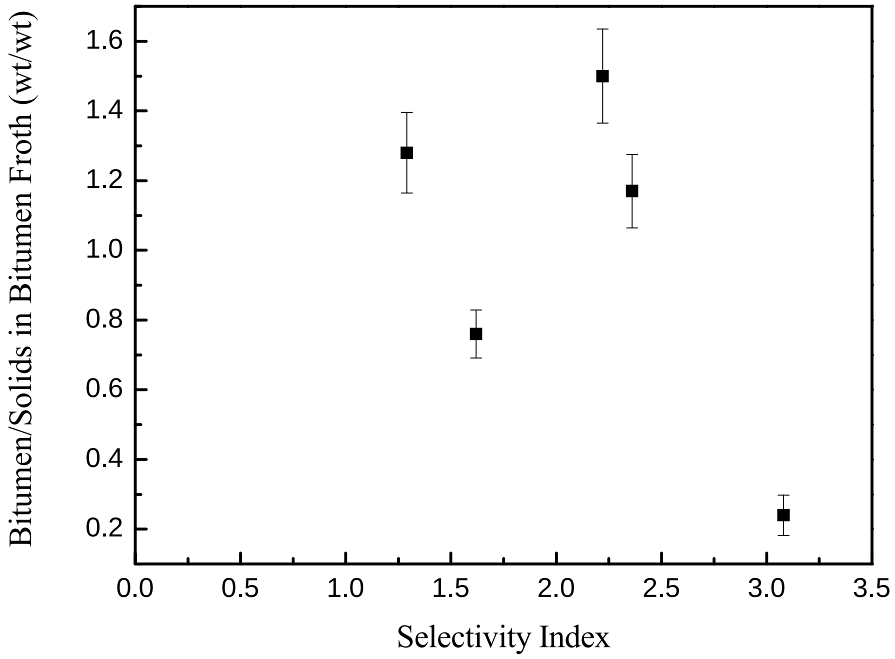

Figure 4-11: Bitumen-to-solids mass ratio in bitumen froth as a function of formation water selectivity index

The comparison in Figure 4-11 shows little correlation between formation water selectivity index and bitumen-to-solids mass ratio in the bitumen froth. It appears that the solids carry-over to bitumen froth does not depend on formation water distribution.

4.5.3.3 Correlation between formation water selectivity index and froth treatment

Percent water was measured at a specific level of diluted bitumen froth and compared with selectivity index of formation water. Bitumen froth from all five ores in this study was treated at the same conditions as description below. The bitumen froth obtained from Denver Cell flotation test was allowed to settle for 24 hours. After draining all the free water, naphtha was added as diluent to 70% mass of bitumen in the froth. In order to ensure that the bitumen was sufficiently mixed with naphtha, the diluted bitumen froth was shaken by a horizontal shaker at low speed for two hours. The diluted bitumen froth was then transferred into a 100 ml graduated cylinder and allowed to settle for one hour.

Coulometric Karl Fischer titration was used to measure water content in oil phase sampled at a specific location in the oil phase. Cou-Lo Aquamax Karl Fisher moisture meter (G.R. Scientific Ltd., UK) was used for this purpose. The instrument works on coulometric principle: equal mole of water reacts with iodine. Therefore, 1 milligram of water will generate 10.71 coulombs of electricity. The titrator determines the water content of the sample by measuring the current of electrolysis necessary to produce the required iodine. The measurement range of water content by this instrument is 1-10 μg, and the maximum sensitivity is 0.1 μg. A syringe was used to collect 0.01-0.05 g sample with the needle tip of syringe being placed at a specific level of 30% below the surface of total diluted bitumen height. The sample-containing syringe was weighed accurately. After adding the sample into Karl Fisher moisture meter, the empty syringe was weighed again to determine the exact mass of the sample added to the titrator. At the end point of titration, the mass of water would be indicated on the titrator screen. Water composition was presented as the mass of water divided by the mass of sample.

To better illustrate the effect of the formation water distribution on the performance of froth treatment, the percent water measured at this specific level is divided by the original percent water in the diluted bitumen froth, which is referred to as emulsion stability ratio in this study. A stability ratio of 1 represents a completely stable emulsion. The percent water at specific level and emulsion stability ratio are given in Table 4-10.

Table 4-10: Percent water in diluted bitumen and emulsion stability ratio

Ore Type	**POSYN**	**TS**	**SYN704**	**Vince A2**	**AL 711**
Percent Water at Specific Level (wt.%)	41	18	22	11	8
Total Percent Water in Diluted Bitumen (wt.%)	51	32	28	21	15
Stability Ratio	0.80	0.56	0.79	0.52	0.53

In Table 4-10, a larger value of stability ratio indicates a stable emulsion. The stability ratio for bitumen froth from the five ores as a function of formation water selectivity index is shown in Figure 4-12.

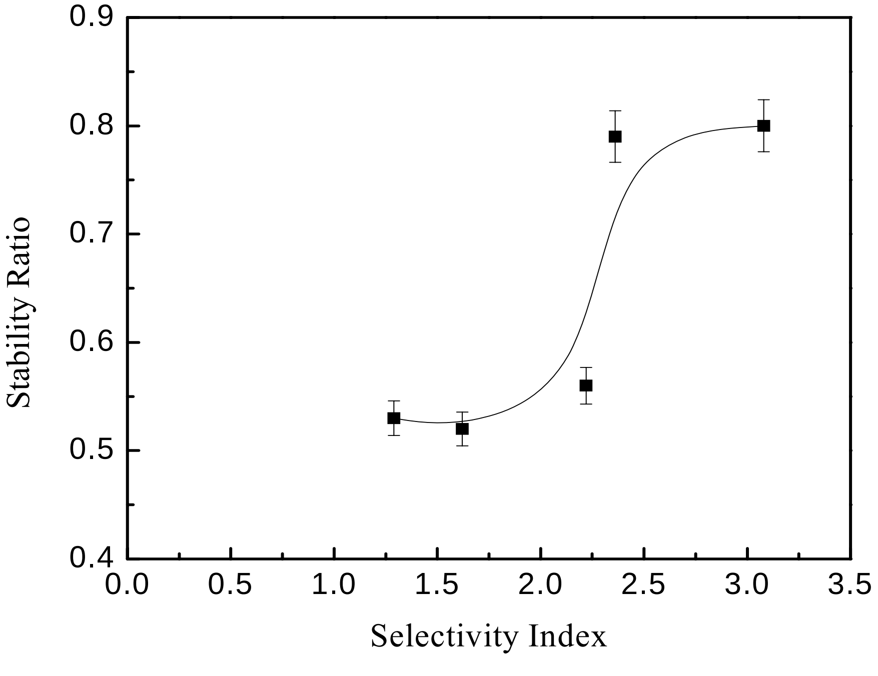

Figure 4-12: Stability ratio as a function of formation water selectivity index

Figure 4-12 shows that an ore with larger selectivity index value exhibits a higher emulsion stability ratio. This finding suggests that for an oil sands ore featuring more preferential distribution of the formation water in bitumen froth, the water in bitumen froth tends to form more stable emulsified water in the froth. On the contrary, for the ore with formation water being distributed evenly during oil sands extraction, the emulsified water droplets in diluted bitumen froth are less stable. It appears that high salt concentration in the formation water is detrimental to froth treatment. Careful inspection of the results reveals that, although TS ore has a low stability ratio, its formation water selectivity index is more than 2. The results in Table 4-9 show the highest bitumen-to-solids mass ratio of bitumen froth from TS ore. The low solids content in bitumen froth leads to low stability ratio of emulsions. This finding serves as enlightenment that the content of solids, especially fines less than 44 μm by diameter, is a more important factor affecting preferential distribution of oil sands formation water in bitumen froth and hence stability of emulsified water.

Chapter 5: Conclusions

In this study, tracer technique as an analysis tool was introduced to determine the formation water distribution during bitumen flotation and to study the effect of formation water in bitumen froth on froth treatment. Two different procedures were employed in the tracer experiments. In the heavy water experiment, heavy water was used as processing water to conduct oil sands extraction tests. The density of separated water samples from flotation extraction was determined by ultrasensitive density meter. In the chemical tracer experiments, Co-EDTA complex was selected as tracer and added to the processing water. The concentration of chemical tracer in bitumen froth water was determined by AAS. From this study, the following conclusions were drawn.

(1) The density technique was not sufficient to achieve definite conclusions. The sensitivity of density instrument had some limitations. The variations of water density during the flotation procedure did not go beyond the minimum error range, making the differentiation of formation water extremely difficult and prone to large errors.

(2) The results of electrical conductivity measurement qualitatively showed that for some ores, the high salinity formation water was preferentially partitioned in the bitumen froth. Due to unquantifiable release of ions during flotation, this method could not provide quantitative analysis on formation water distribution.

(3) Co-EDTA complex could be used as chemical tracer for tracking the formation water distribution. First, cobalt could be detected with high accuracy by Atomic Absorption Spectroscopy. Second, the complex of Co^{2+} and EDTA was absent in the ores and did not interfere with bitumen recovery. In the complex form of Co^{2+} and EDTA, it did not react with oil sands components during extraction as confirmed by mass balance tests.

(4) For both poor and rich ores, the formation water did not uniformly distribute during oil sands extraction. Distribution of formation water as emulsified water was higher than that of processing water as emulsified water in the bitumen froth.

(5) The selectivity index of formation water, defined as the percent formation water in emulsified water divided by the percent formation water in an even distribution case, was a good measure of formation water distribution. It correlated well with the grade of oil sands ores. The poor ore featuring low bitumen content, high water content and high fines content exhibited a high formation water selectivity index which indicates a more preferential distribution of formation water in emulsified water of bitumen froth.

(6) Among other oil sands characteristics, the percent fines of an oil sands ore was an important factor in determining formation water distribution. For high fines ore, its percent formation water in emulsified water was high; for low fines ore, its percent formation water in emulsified water was low, close to even distribution or well mixed condition with processing water.

(7) The large formation water selectivity index appeared to be beneficial to the bitumen recovery, but to lower froth quality, measured by low bitumen-to-solids mass ratio and low bitumen-to-water mass ratio in bitumen froth.

(8) An oil sands ore of higher formation water selectivity index featured more stable emulsified water in diluted bitumen. The ore with formation water being distributed evenly in all streams of oil sand extraction system, on the other hand, exhibited less stable emulsified water in diluted bitumen froth. It appeared that high salt concentration in the formation water was detrimental to froth treatment.

Chapter 6: Recommendations for Future Study

(1) Heavy organic components (e.g. asphaltenes, resins, saturates, and aromatics) in the bitumen are other important factors to make the emulsified water stable. Heavy organic component content should be analyzed for different ores, and the correlation with formation water distribution in bitumen froth and stability of emulsified water should be established.

(2) In this study all the bitumen froth was not treated, except for addition of naphtha as diluent. In industry, the froth is treated by going through several dehydration methods such as inclined plate settling, centrifuge dewatering and demulsifier addition. After froth treatment there is still about 2% emulsified water remaining in bitumen product. Therefore in a future study, the froth should be treated by following industry conditions, and the water remained in the froth, which is the hardest to get rid of, should be separated and analyzed.

(3) The oil sands flotation process should be conducted with different pH values of processing water.

(4) Wettability of fines to be analyzed to understand the observed positive correlation between percent fines and selectivity index of formation water in bitumen froth and the mechanism of preferential distribution of formation water in bitumen froth.

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Appendix

Table A-1: The feed and water used in oil sands extraction for five ores (all in g)

POSYN	**Test 1**	**Test 2**	**Test 3**	**Average**
Processing Water	400.01	400.10	400.48	400.20
Ore	130.00	130.01	130.03	130.01
Formation Water	9.66	9.66	9.66	9.66
Total Water	409.67	409.76	410.14	409.86
TS				
Processing Water	400.04	400.09	400.10	400.08
Ore	130.00	130.05	130.06	130.04
Formation Water	12.18	12.19	12.19	12.19
Total Water	412.22	412.28	412.29	412.26
SYN704				
Processing Water	408.47	408.46	400.00	405.64
Ore	130.06	130.02	130.01	130.03
Formation Water	7.02	7.02	7.02	7.02
Total Water	415.49	415.48	407.02	412.66
Vince A2				
Processing Water	400.01	400.08	400.03	400.04
Ore	130.00	130.01	130.03	130.01
Formation Water	4.07	4.07	4.07	4.07
Total Water	404.08	404.15	404.10	404.11
AL 711				
Processing Water	400.02	400.08	400.03	400.04
Ore	130.11	130.02	130.01	130.05
Formation Water	3.55	3.55	3.55	3.55
Total Water	403.57	403.63	403.58	403.59

Table A-2: Water source of emulsified water, free water and tailings water for POSYN ore

POSYN ore	**Co (ppm)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Processing Water	36.6	37.8	36.9	37.1
Formation Water	0.0	0.0	0.0	0.0
Emulsified Water	34.3	34.9	34.0	34.4
Free Water	35.8	37.1	35.9	36.3
Tailings Water	35.7	36.9	36.1	36.2
Well Mixed	35.7	36.9	36.0	37.1
Emulsified Water	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	6.28	7.67	7.86	7.27
Arising from Processing Water	93.72	92.33	92.14	92.73
Free Water	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	2.19	1.85	2.71	2.25
Arising from Processing Water	97.81	98.15	97.29	97.75
Tailings Water	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	2.46	2.38	2.17	2.34
Arising from Processing Water	97.54	97.62	97.83	97.66
Well-Mixed	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	2.36	2.36	2.36	2.36
Arising from Processing Water	97.64	97.64	97.64	97.64

Table A-3: Formation water and processing water distribution for POSYN ore

Total Water	**Emulsified Water**	**Free Water**	**Tailings Water**	**Total Water**
Mass(g)	27.33	71.31	307.26	405.9
Water Distribution	6.73%	17.57%	75.70%	100%
	Water Source for Different Water Streams			
	Emulsified Water	**Free Water**	**Tailings Water**	
Percent of Formation Water	7.27%	2.25%	2.34%	
Percent of Processing Water	92.73%	97.75%	97.66%	
	Mass of Water in Different Streams (g)			
	Emulsified Water	**Free Water**	**Tailings Water**	
Arising from Formation Water	1.99	1.60	7.18	
Arising from Processing Water	25.34	69.71	300.08	
	Water Distribution			
	Emulsified Water	**Free Water**	**Tailings Water**	**Total Water**
Formation	18.46%	14.89%	66.65%	100%
Processing	6.41%	17.64%	75.95%	100%

Table A-4: Water source of emulsified water, free water and tailings water for TS ore

TS ore	Co (ppm)			
	Test 1	Test 2	Test 3	Average
Processing Water	36.6	38.1	37.5	37.4
Formation Water	0.0	0.0	0.0	0.0
Emulsified Water	34.6	35.5	34.7	34.9
Free Water	35.2	36.8	36.2	36.1
Tailings Water	35.4	37.0	36.3	36.2
Well-Mixed	35.5	37.0	36.4	36.3
Emulsified Water	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	5.46	6.82	7.47	6.59
Arising from Processing Water	94.54	93.18	92.53	93.41
Free Water	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	3.83	3.41	3.47	3.57
Arising from Processing Water	96.17	96.59	96.53	96.43
Tailings Water	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	3.28	2.89	3.20	3.12
Arising from Processing Water	96.72	97.11	96.80	96.88
Well-Mixed	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	2.95	2.96	2.96	2.96
Arising from Processing Water	97.05	97.04	97.04	97.04

Table A-5: Formation water and processing water distribution for TS ore

Total Water	**Emulsified Water**	**Free Water**	**Tailings Water**	**Total Water**
Mass(g)	15.64	52.56	340.63	408.83
Water Distribution	3.83%	12.85%	83.32%	100%
	Water Source for Different Water Streams			
	Emulsified Water	**Free Water**	**Tailings Water**	
Percent of Formation Water	6.58%	3.57%	3.12%	
Percent of Processing Water	93.42%	96.43%	96.88%	
	Mass of Water in Different Streams (g)			
	Emulsified Water	**Free Water**	**Tailings Water**	
Arising from Formation Water	1.03	1.88	10.63	
Arising from Processing Water	14.61	50.68	330.00	
	Water Distribution			
	Emulsified Water	**Free Water**	**Tailings Water**	**Total Water**
Formation	7.61%	13.88%	78.51%	100%
Processing	3.70%	12.82%	83.48%	100%

Table A-6: Water source of emulsified water, free water and tailings water for SYN 704 ore

SYN 704 ore	**Co (ppm)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Processing Water	40.7	41.3	42.4	41.5
Formation Water	0.0	0.0	0.0	0.0
Emulsified Water	39.1	39.7	40.6	39.8
Free Water	39.7	40.4	41.6	40.6
Tailings Water	40.1	40.6	41.8	40.8
Well-Mixed	40.0	40.6	41.7	41.5
Emulsified Water	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	3.93	3.87	4.25	4.02
Arising from Processing Water	96.07	96.13	95.75	95.98
Free Water	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	2.46	2.18	1.89	2.17
Arising from Processing Water	97.54	97.82	98.11	97.83
Tailings Water	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	1.47	1.69	1.42	1.53
Arising from Processing Water	98.53	98.31	98.58	98.47
Well-Mixed	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	1.69	1.69	1.72	1.70
Arising from Processing Water	98.31	98.31	98.28	98.30

Table A-7: Formation water and processing water distribution for SYN 704 ore

Total Water	**Emulsified Water**	**Free Water**	**Tailings Water**	**Total Water**
Mass(g)	17.23	56.61	335.64	409.48
Water Distribution	4.21%	13.82%	81.97%	100%
	Water Source for Different Water Streams			
	Emulsified Water	**Free Water**	**Tailings Water**	
Percent of Formation Water	4.02%	2.17%	1.53%	
Percent of Processing Water	95.98%	97.83%	98.47%	
	Mass of Water in Different Streams (g)			
	Emulsified Water	**Free Water**	**Tailings Water**	
Arising from Formation Water	0.69	1.23	5.13	
Arising from Processing Water	16.54	55.38	330.51	
	Water Distribution			
	Emulsified Water	**Free Water**	**Tailings Water**	**Total Water**
Formation	9.81%	17.45%	72.74%	100%
Processing	4.11%	13.76%	82.13%	100%

Table A-8: Water source of emulsified water, free water and tailings water for Vince A2 ore

Vince A2 ore	**Co (ppm)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Processing Water	37.2	38.3	40.5	38.7
Formation Water	0.0	0.0	0.0	0.0
Emulsified water	36.5	37.7	39.9	38.0
Free Water	36.6	37.7	40.1	38.1
Tailings Water	36.8	37.9	40	38.2
Well-Mixed	36.8	37.9	40.1	38.7
Emulsified Water	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	1.88	1.57	1.48	1.64
Arising from Processing Water	98.12	98.43	98.52	98.36
Free Water	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	1.61	1.57	0.99	1.39
Arising from Processing Water	98.39	98.43	99.01	98.61
Tailings Water	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	1.08	1.04	1.23	1.12
Arising from Processing Water	98.92	98.96	98.77	98.88
Well-Mixed	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	1.01	1.01	1.01	1.01
Arising from Processing Water	98.99	98.99	98.99	98.99

Table A-9: Formation water and processing water distribution for Vince A2 ore

Total Water	Emulsified Water	Free Water	Tailings Water	Total Water
Mass(g)	16.4	53.91	330.67	400.98
Water Distribution	4.09%	13.44%	82.47%	100%
	Water Source for Different Water Streams			
	Emulsified Water	**Free Water**	**Tailings Water**	
Percent of Formation Water	1.64%	1.39%	1.12%	
Percent of Processing Water	98.36%	98.61%	98.88%	
	Mass of Water in Different Streams (g)			
	Emulsified Water	**Free Water**	**Tailings Water**	
Arising from Formation Water	0.27	0.75	3.70	
Arising from Processing Water	16.13	53.16	326.97	
	Water Distribution			
	Emulsified Water	**Free Water**	**Tailings Water**	**Total Water**
Formation	5.72%	15.88%	78.40%	100%
Processing	4.07%	13.42%	82.51%	100%

Table A-10: Water source of emulsified water, free water and tailings water for AL 711 ore

AL 711 ore	**Co (ppm)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Processing Water	42.3	39.4	41.5	41.1
Formation Water	0.0	0.0	0.0	0.0
Emulsified Water	41.9	39	40.9	40.6
Free Water	41.8	39	41.1	40.6
Tailings Water	41.9	39.1	41.1	40.7
Well-Mixed	41.9	39.1	41.1	41.1
Emulsified Water	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	0.95	1.02	1.45	1.14
Arising from Processing Water	99.05	98.98	98.55	98.86
Free Water	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	1.18	1.02	0.96	1.05
Arising from Processing Water	98.82	98.98	99.04	98.95
Tailings Water	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	0.95	0.76	0.96	0.89
Arising from Processing Water	99.05	99.24	99.04	99.11
Well-Mixed	**Percent of Water (%)**			
	Test 1	**Test 2**	**Test 3**	**Average**
Arising from Formation Water	0.88	0.88	0.88	0.88
Arising from Processing Water	99.12	99.12	99.12	99.12

Table A-11: Formation water and processing water distribution for AL 711 ore

Total Water	**Emulsified Water**	**Free Water**	**Tailings Water**	**Total Water**
Mass(g)	13.51	52.96	334.52	400.99
Water Distribution	3.37%	13.21%	83.42%	100%
	Water Source for Different Water Streams			
	Emulsified Water	**Free Water**	**Tailings Water**	
Percent of Formation Water	1.14%	1.05%	0.89%	
Percent of Processing Water	98.86%	98.95%	99.11%	
	Mass of Water in Different Streams (g)			
	Emulsified Water	**Free Water**	**Tailings Water**	
Arising from Formation Water	0.15	0.56	2.98	
Arising from Processing Water	13.36	52.40	331.54	
	Water Distribution			
	Emulsified Water	**Free Water**	**Tailings Water**	**Total Water**
Formation	4.07%	15.18%	80.76%	100%
Processing	3.36%	13.19%	83.45%	100%

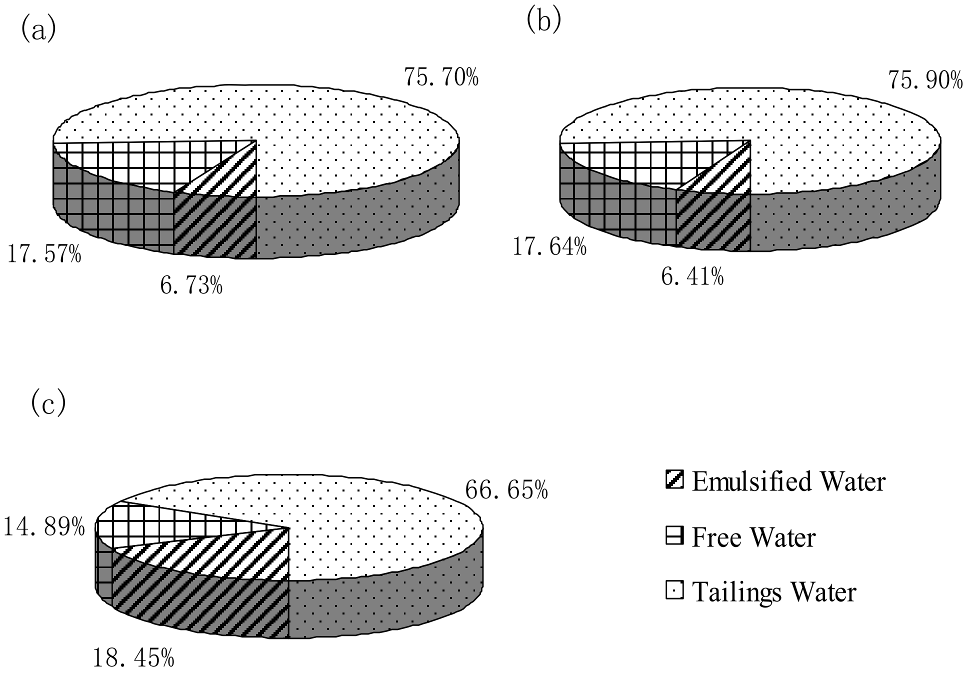

Figure A-1: (a) Total water distribution; (b) Processing water distribution; (c) Formation water distribution. (POSYN ore)

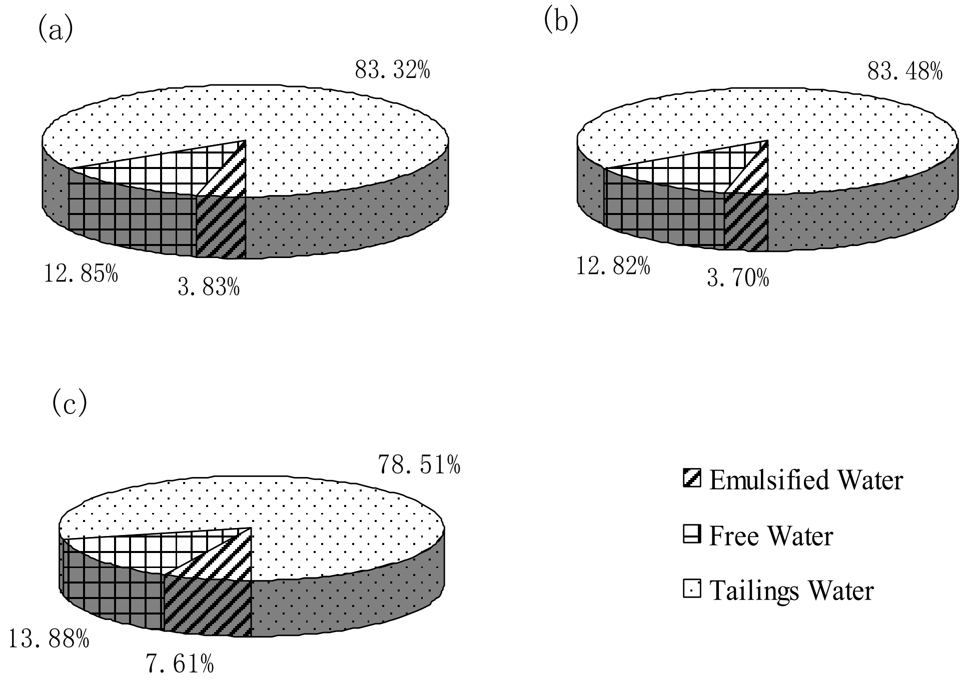

Figure A-2: (a) Total water distribution; (b) Processing water distribution; (c) Formation water distribution. (TS ore)

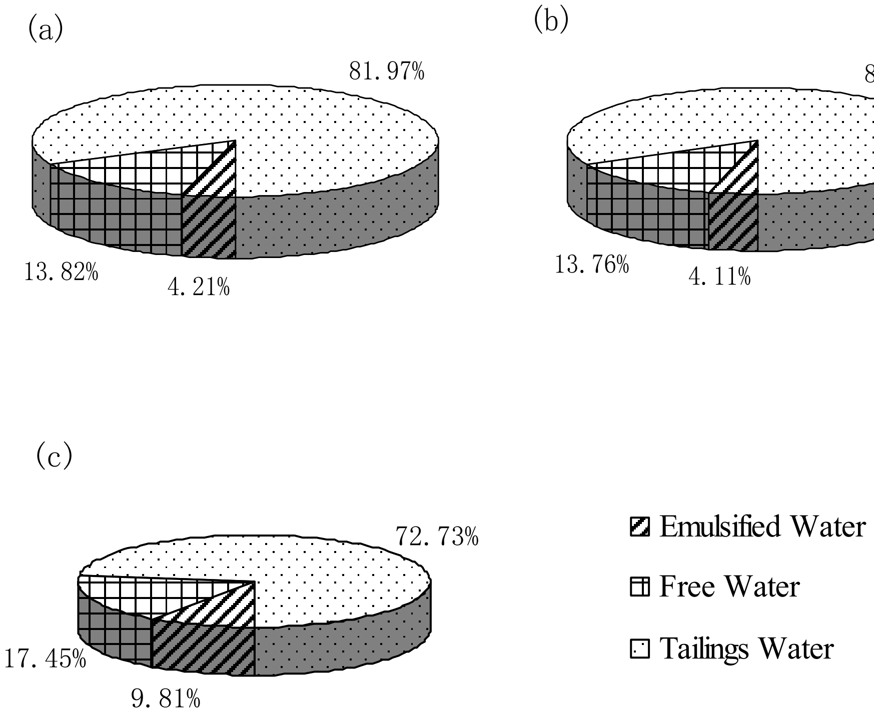

Figure A-3: (a) Total water distribution; (b) Processing water distribution; (c) Formation water distribution. (SYN 704 ore)

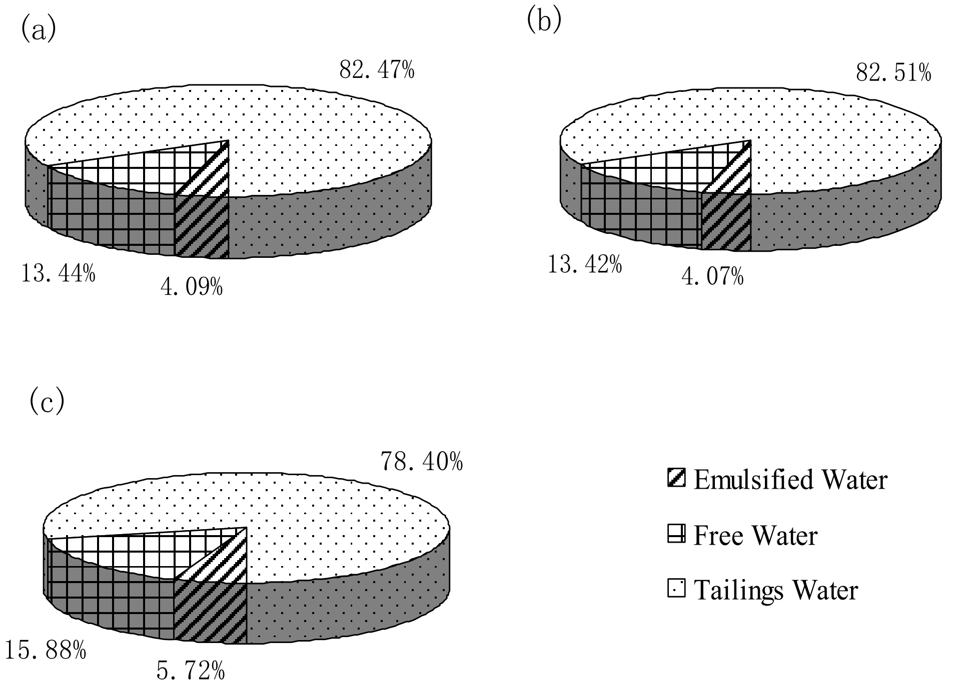

Figure A-4: (a) Total water distribution; (b) Processing water distribution; (c) Formation water distribution. (Vince A2 ore)

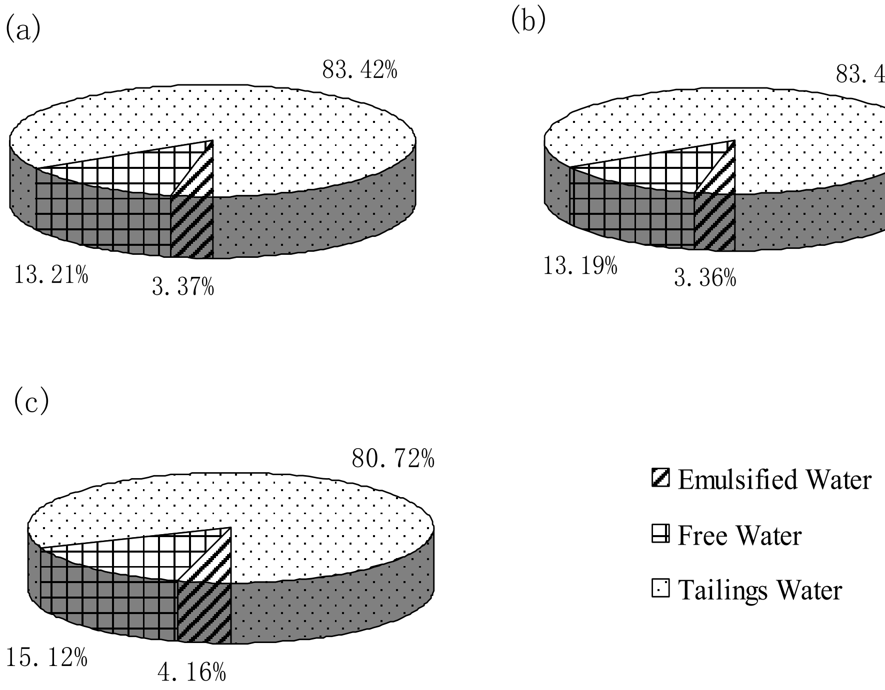

Figure A-5: (a) Total water distribution; (b) Processing water distribution; (c) Formation water distribution. (AL 711 ore)