"Nothing in life is to be feared. It is only to be understood"

Marie Curie

"A dream becomes a goal when action is taken toward its achievement"

Bo Bennett

UNIVERSITY OF ALBERTA

Role of Fine Clays and Ionic Species in Bitumen Extraction from Oil Sands Ores using the Hot Water Extraction Process

By

Tshitende Kasongo ©

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ABSTRACT

The Alberta oil Sands are mined in Fort McMurray to recover bitumen by flotation. For good processing ores, bitumen recovery is higher than 92% but lower than 70% for poor ores. We have identified that the depression of bitumen recovery results from the loss of bitumen hydrophobicity due to the interactions between calcium and magnesium ions in water and montmorillonite clays in the ores. We have also established that bitumen recovery correlated with the receding water contact angle.

Our contribution to explain depression of bitumen recovery was based on doping tests that consists in poisoning good processing ores samples with additives to make them behave like poor processing ores. Our imaging technique allowed visualizing the results of doping tests on bitumen-air bubbles attachment. We have found that individual additives had marginal effect on bitumen recovery, but bitumen recoveries were decreased when montmorillonite clay at 1 wt % of the oil sands ore and calcium or magnesium ions at 40 ppm in the feed water were present together; that depression of bitumen recovery depended on the valence and concentrations of cations, on the type and concentration of clays than on the ionic strength of the slurries, that bitumen recovery was sensitive to temperature variations only below 50°C and that bitumen recovery was affected by the mechanical energy provided by the agitation.

Depression of bitumen recovery was due to the bridging of divalent calcium ions that interact with carboxylic groups of natural surfactants on the surface of bitumen and with montmorillonite clay particles. They form a slime coating barrier that is confirmed by the use of the Atomic Force Microscopy and by the induction time

techniques. The slime coating masks bitumen surface, and prevents its attachment to air bubbles, resulting in poor bitumen floatability and thereby in depressed bitumen recovery.

Our finding suggests that the effect of calcium ion in water would not be observed for low fine contents oil sands ores. Addition of sodium hydroxide at 0.04 % of the oil sands ores corrected the depression of bitumen recovery from depressed good processing ore but not for poor ore samples. Addition of sodium bicarbonate at 1000 ppm prevented depression of bitumen recovery by softening feed water but did not restore bitumen recovery once depressed.

More work on more operating variables is still needed to expand our understanding of the mechanisms of depression of bitumen recovery and to find synergy required to prevent clays from interacting with metal ions and therefore to minimize of depression of bitumen from poor processing ore during flotation.

ACKNOWLEDGEMENT

I express sincere appreciation and many thanks to my supervisors, Dr. Jozef Szymanski and Dr. Zhenghe Xu, for their support and encouragement during this research work, for their enthusiasm towards advising me in doing research work and in teaching the details of this project. Their sharp insight and expertise in oil sands extraction are invaluable in helping me throughout this research work. I am indebted to Dr. Jacob Masliyah and Dr. S Wanke for helping me to start this research program. I would like also to thank my colleagues at the University of Alberta for their support through discussion and laboratory work.

This study was possible due to the financial assistance provided by the National Science and Engineering Research Council (NSERC), the NSERC Industrial Research Chair in Oil Sands Engineering held by Dr. Masliyah, the University of Alberta and by my employers during this research work: Albian Sands Energy Inc. and Petro-Canada MacKay River SAGD Project.

I wish to thank my parents, to whom this thesis is dedicated, for their encouragement and sacrifice to allow me to achieve this level.

Finally, I wish to thank my wife, Mpiana and my children, for their understanding, patience and encouragement that I needed to start this program after so many years away from the academics.

DEDICATION

To the memory of my affectionate parents, my mother Mujinga Kupa-Kupanga, my father Kabata Musaka, my brothers and my sisters.

To my wife Mpiana and my children.

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LIST OF SYMBOLS

A	surface area in a wire frame formed with a film of detergent in water
D	particle diffusion constant
dA	new expanded surface area,
d_F	Feret bubble diameter
dw	work exerted by applying a force
dx	distance change
E	applied electric force field (volts/meter) on the double layer of the particles
f	bitumen grade of flotation feed sample (Eq. 3-3)
F	force to the movable side of the frame (Eq. 2-8)
F	mass of the flotation feed sample (Eq 3-2)
F_i	mass of froth samples at time i
f_i	bitumen grades of froths collected at time i
f_p	primary froth grade (10 minutes) (Eq. 3-11)
f_{ps}	grade of the combined primary and secondary froth
f_t	grade of the total froth including the wall froth recovered (Eq. 3-13)
t	flotation time 2, 3, 5, minutes, S (secondary), W (wall froth) and tailings (T)
l	length of a ring of radius R (Eq. 2-10)
l	length of the area A (Eq. 2-10)
Q	the froth quality or bitumen grade of flotation froth
R	first order rate bitumen recovery (%) at time t (Eq. 3-1 and 4-1))
R	radius of the ring in the Whilelmy process (Eq. 2-12)
R_∞	bitumen recovery at time infinite (%)
R_t	incremental bitumen recoveries at flotation time t

R_M	maximum bitumen recoveries achievable over entire flotation time
R_p	primary bitumen recovery
R_s	secondary bitumen recovery
R_t	total bitumen recovery including the wall froth recovered
x	width of the area A

Greek Symbols

θ	equilibrium contact angle
η	viscosity of the fluid
σ	surface tension or energy per unit area in mJ/ m^2 to create new surfaces
κ	the flotation rate constant (min^{-1}) (Eq. 3-9)
τ	zero time correction factor (min)
υ	particle constant velocity (meter/sec) with respect to the electrolyte
θ_a	advancing contact angle at the advancing edge
σ_{ab}	surface tension of bitumen
σ_{aw}	surface tension of water
σ_{bw}	water-bitumen interfacial tension
$\theta_{hysteresis}$	contact angle hysteresis
ε	dielectric contant
ε_o	permittivity of vacuum
θ_r	receding contact angle at the receding edge of the liquid drop
ζ	zeta potential

CHAPTER 1

INTRODUCTION

Oil sands ores are mined in Alberta to recover bitumen; their composition is a mixture of mainly quartz and bitumen. Bitumen is the economic product that is upgraded into synthetic crude oil that is fed to refineries to produce gasoline, jet fuel, heating oil and diesel fuel. The Alberta oil sands resources cover 141,000 square kilometers of leases, concentrated mainly in the Athabasca, Peace River, Wabasca, and Cold Lake regions in the province. The location index of oil sands deposits in Alberta is given in Figure 1-1 (Camp, 1976 and 1977; Cameron Engineers, 1978; Paul, 2002). The bitumen contained in this region is over 1.3 trillion barrels of crude oil equivalent (Morgan, 2001; Sparks, 2003). The estimated reserve is evaluated at 869 billion barrels of bitumen of which 60 billion barrels are recoverable using surface mining techniques (O'Carroll, 2000). The Athabasca resources represent the largest deposit of bitumen from one sole location in the world (Alberta Energy, 2002). These resources are larger than Saudi Arabia's total proven oil reserves, making Canada one of the biggest bitumen producers (Masliyah, 2003). With new oil sands companies in operation, more than 50% of oil production in Canada will originate from the oil sands processing by 2010. In the Fort McMurray oil sands industry, Suncor Energy Inc., Syncrude Canada Ltd. and Albian Sands Energy Inc. together process over one million tons of oil sand ores to produce over 700,000 Bbl of bitumen per day. These operations constitute one of the largest concentrations of mining and processing activities in the world.

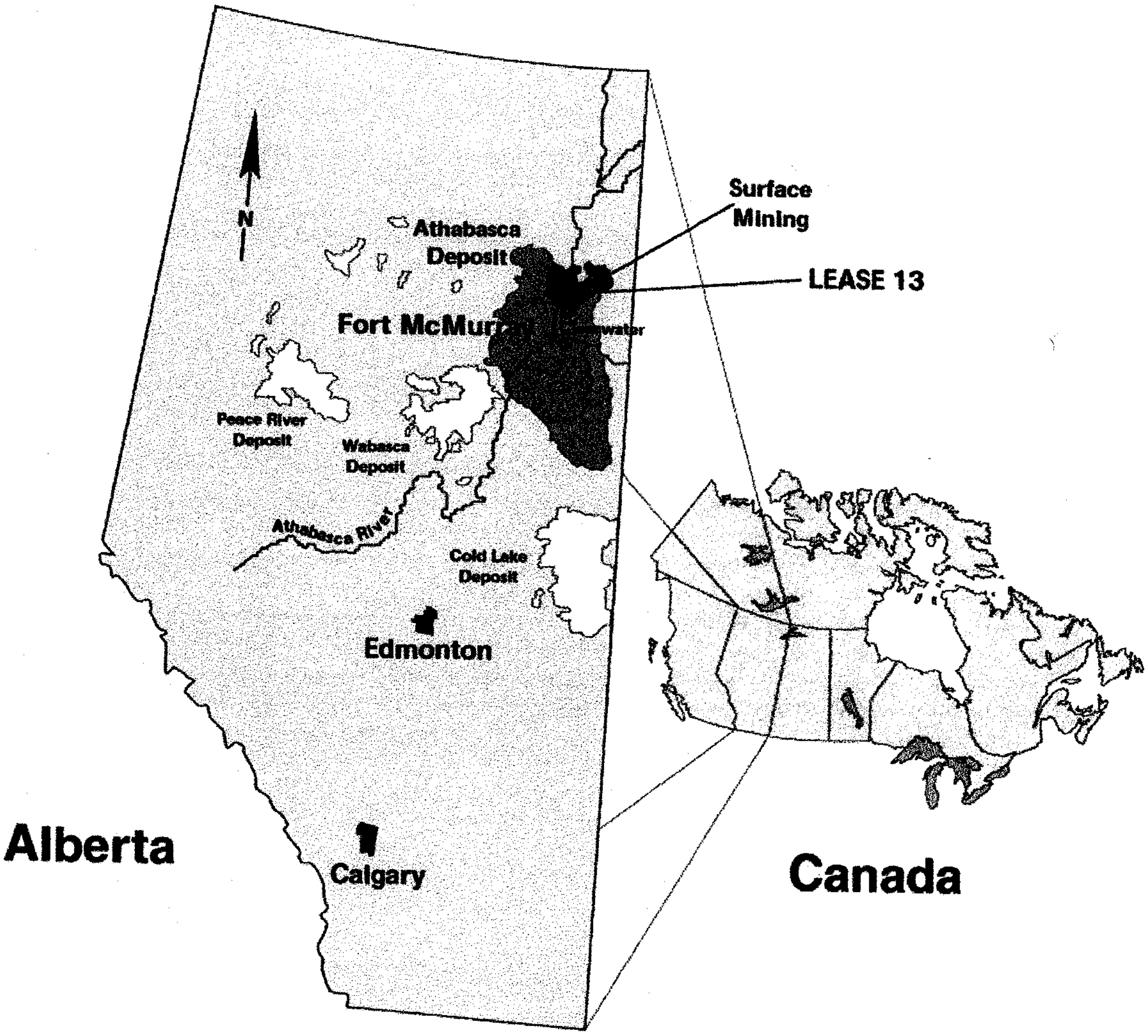


Figure 1-1: Location index of oil sands deposits in Alberta

Bitumen is a viscous mixture of high molecular weight hydrocarbons. In the oil sands, it is a sticky material on the surface of sand grains. Bitumen in oil sands is distributed throughout an unconsolidated mineral matrix and it resists flowing and separating from sand surfaces at ambient temperature. After mining, the processing operations consist of ore preparation, extraction, froth treatment and upgrading. Two extraction technologies currently used are the Clark Hot Water Extraction (CHWE) Process developed by K. A. Clark in the 1920's (Clark and Pasternak, 1932; Hepler and Smith, 1994), and the Low Energy Extraction (LEE) Process. Flow charts of Syncrude Canada (Figure 1-2) and Albian Sands Energy (Figure 1-3) depict the two industrial technologies.

Oil sands ores do not require communition to separate/liberate its components by size reduction. At present, the commercial Athabasca oil sand industries operate using mainly open pit mining and rolling crushers to break coarse lumps of ore (O'Carroll, 2000). The ore is then conditioned either with caustic addition at high temperature (80°C) using tumblers in the Clark Hot Water Extraction processes (Clark, 1944; Camp, 1976), or without caustic addition at lower temperature (40°C) known as the Low Energy Extraction Process (FTFC, 1995). Extraction processes, based on proven mineral processing technologies and on hydro transport pipelines with air injection are used to condition the slurry. A water-based gravity separation technique and flotation processes are used to separate bitumen into froth and to reject sands as tailings (Kessick, 1978). Extracted bitumen froths are deaerated and diluted with solvents. Water and solids are removed from diluted bitumen using inclined plate settlers and centrifugation in the Syncrude and Suncor practices, or in counter current decantation settlers with precipitation of high molecular weight asphaltene components in the Albian Sands

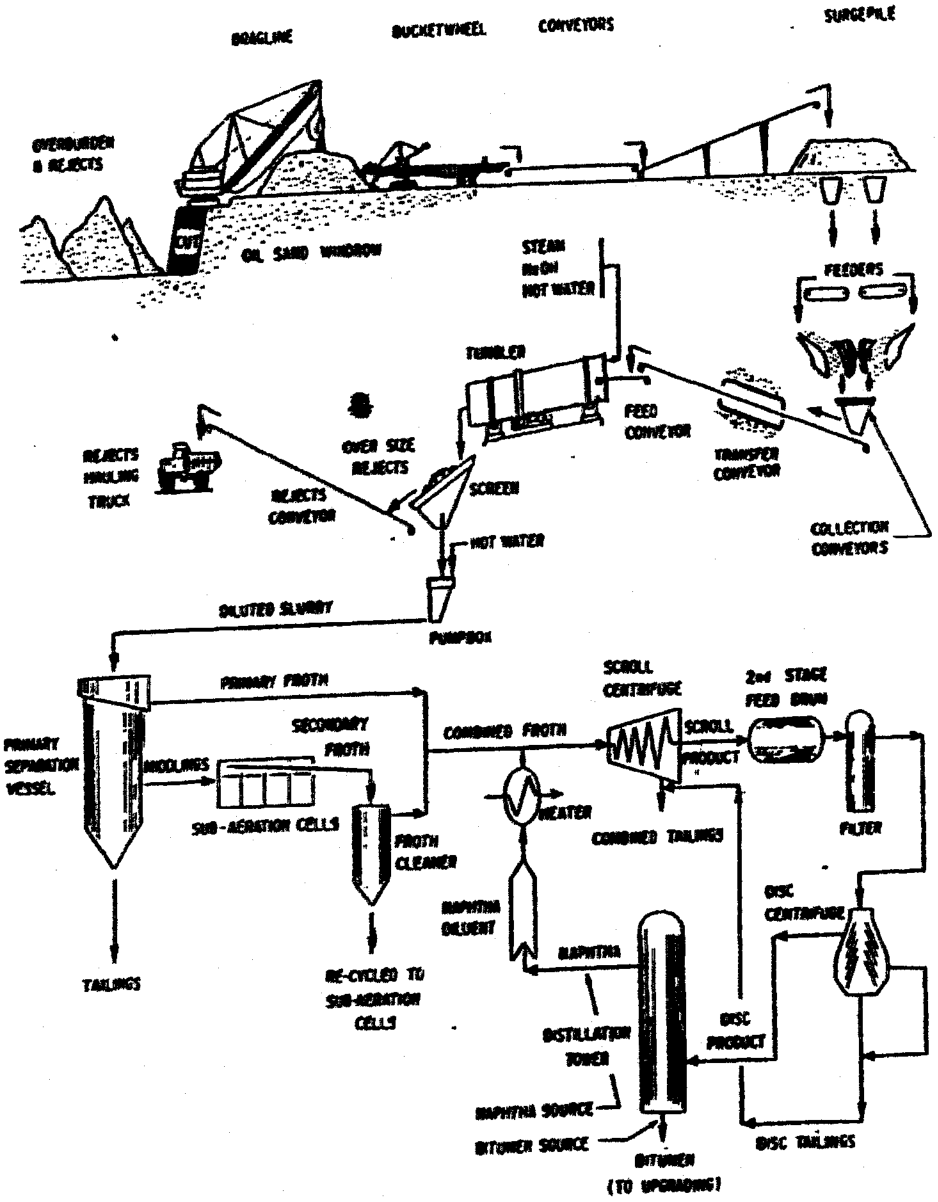


Figure 1-2: A generic flowsheet for oil sands extraction at Syncrude Canada

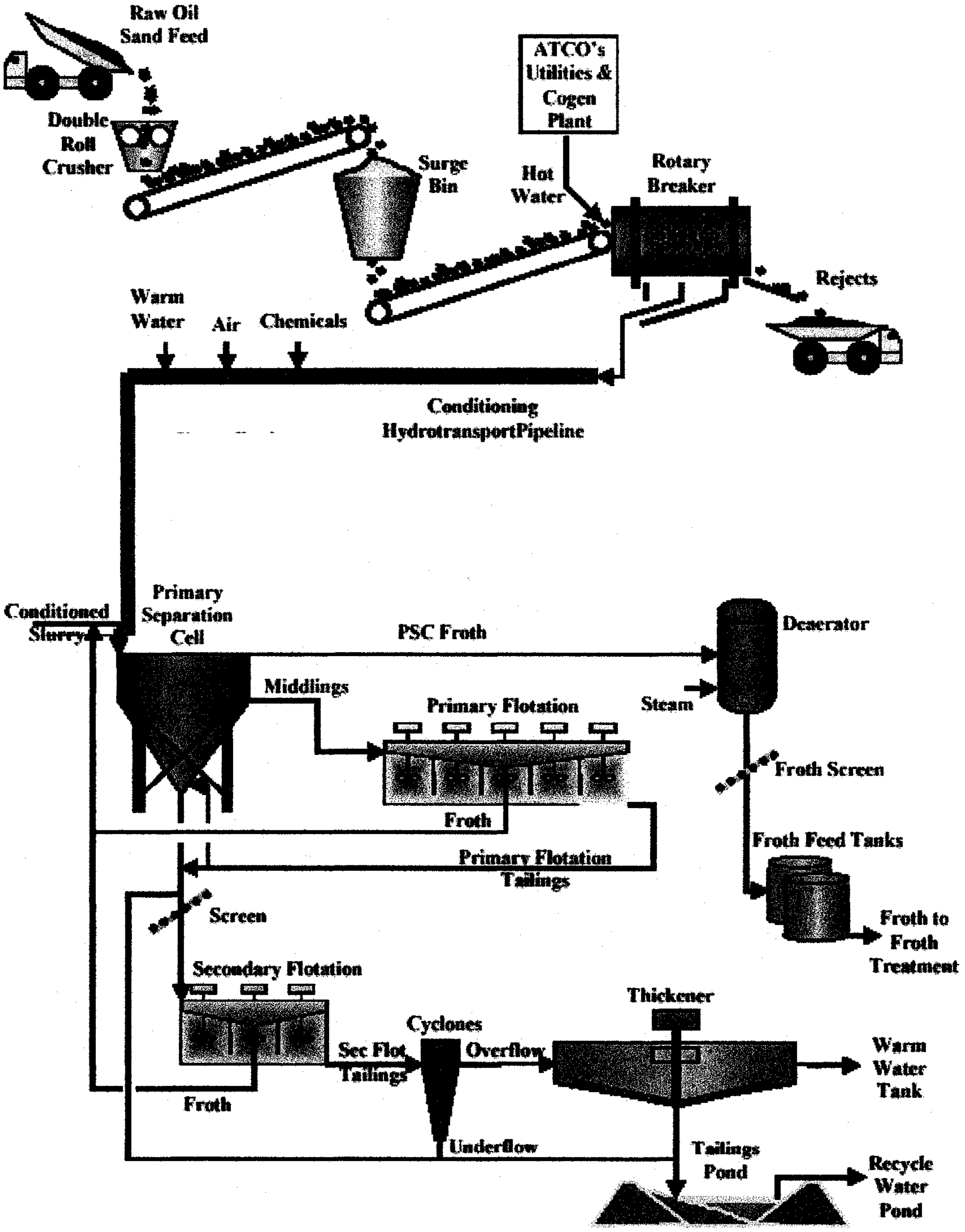


Figure 1-3: Ore prep and extraction process at Albian Sands Energy Inc.

process (Albian Sands, 2001). Hydro cracking technologies are used to convert bitumen into upgraded synthetic crude oil as feedstock for refining to produce petroleum derivatives. In general, with efficient separation processes, more than 92% of the bitumen content of an ore is recovered as a froth containing about 60% bitumen, 30% water and 10% solids (Masliyah, 2003). However, bitumen recovery below 50% is not uncommon in practice when certain types of ores are processed. Bitumen is also extracted in-situ by steam injection into the ore body (Mathieson and Stenason, 2001) using the so-called Steam Assisted Gravity Drainage (SAGD) process (Nasr, 2003; Thimm, 2003). This technique is used by Petro-Canada at its MacKay River Project in Fort McMurray. SAGD process involves two horizontal wells drilled into the productive reservoir. Steam is injected in the top well to create a hot chamber and its condensate will drain the heated bitumen down under gravity into the bottom well where the emulsion will, under pressure, flow back to the processing plant on surface.

1.1 Good and Poor Processing Ores

Operations personnel and researchers have found that the efficiency of extraction processes depends on a myriad of operating factors related not only to ore characteristics, but also to water chemistry, operating conditions, and chemical additions as summarized in Table 1-1.

It has been observed that changes in these parameters affect the efficiency of bitumen separation and the selectivity of separation, resulting in a new classification of refractory ores that encompass poorly processing ores, problem ores, transition ores, oxidized ores, and low grade ores. Depression of bitumen recovery and production of poor quality froth characterize these types of ores. Extensive work has been undertaken to identify the parameters that affect bitumen recovery and froth quality during extraction of bitumen from poor processing ores, and to understand mechanisms associated with depression of bitumen recovery. However, the progress has been slow because of the complex nature of ore, the number of variables involved during extraction, and the complexity of extraction processes.

Table 1-1: Factors affecting hot water extraction processes

Ore characteristics	Water chemistry	Operating conditions	Chemical additives
• Fine content • Physical Property of fines • Grade (good, poor) • Bitumen composition • Aging of ores • Type of fines	• Type of metal ions • Metal ion content • Polyelectrolyte • Carbonate concentration • Surfactant • pH	• Temperature • Mechanical mixing • Slurry density • Residence time • Aeration	• Caustic • LEE chemicals • Dispersants • Polymers

The bitumen grade and its fine mineral content characterize the processability of an ore. Ore deposits vary in composition and processability from one mine to another and even within the same mine locations (Paul, Albian Sands, 2003; Masliyah, 2003). Arbitrarily, ore with a bitumen grade that is higher than 10% bitumen by weight is considered high grade ore. Oil sands ore containing between 10% and 8% bitumen is considered middle grade ore, while ore containing less than 8% bitumen is considered low grade ore. This classification is depicted in Figure 1-4 that shows that typically high grade ores contain low fines and they produce high recoveries ranging between 90-95% as shown in Figure 1-5 (Cuddy, 2000) and Figure 1.6 (Wallace, 2000). These figures show also that low grade ores contain high fines and processing it results in bitumen recoveries lower than 70% and poor froth quality. Under certain processing conditions, high grade ores could behave like poor processing ores, resulting in low bitumen recovery and poor froth quality.

1.2 Parameters that Depress Bitumen Recovery

Although extensive efforts have been devoted to studies of interactions between bitumen and clays or between bitumen and metal ions, little emphasis has been placed on interactions between bitumen and clays in the presence of metal ions. To understand collectively the role of fines and metal ions in bitumen extraction, it has been observed through research efforts and in operating plants as suggested in Figure 1-5 by Cuddy (2000) that divalent metal ions, such as calcium and magnesium, depress bitumen recovery for some ores. This empirical relationship between bitumen recoveries and divalent ions for low and high fine oil sands ores in commercial operations is extended beyond the limits of our testing conditions by mapping bitumen recoveries as shown in

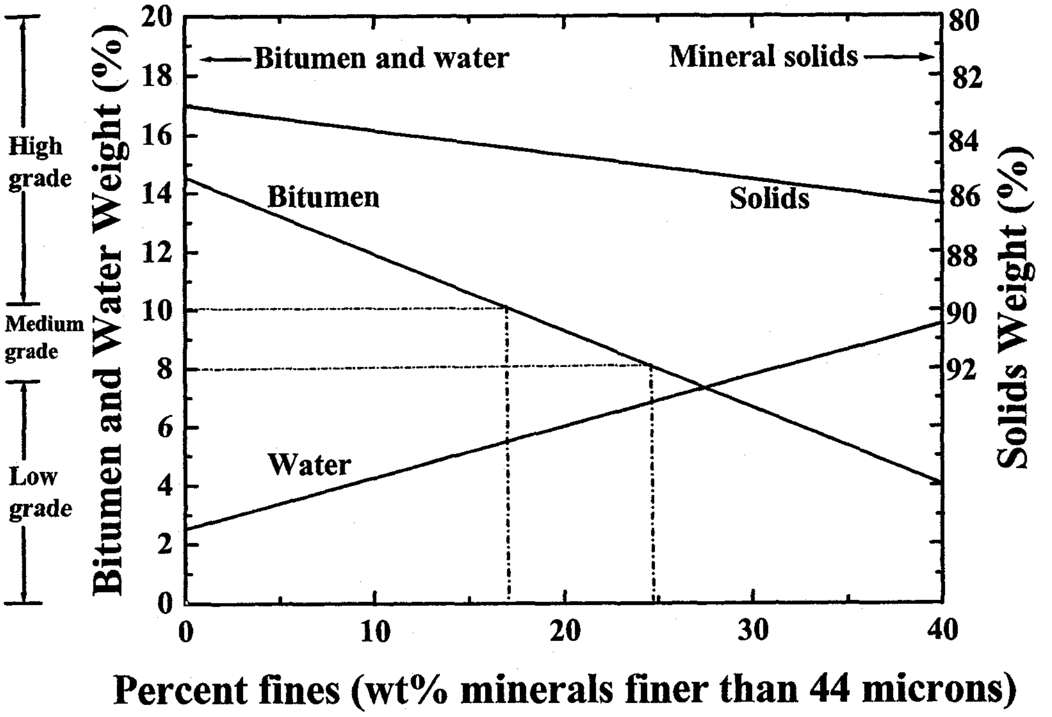


Figure 1-4: Composition and classification of oil sand ores on the basis of percent fines after Masliyah (1999)

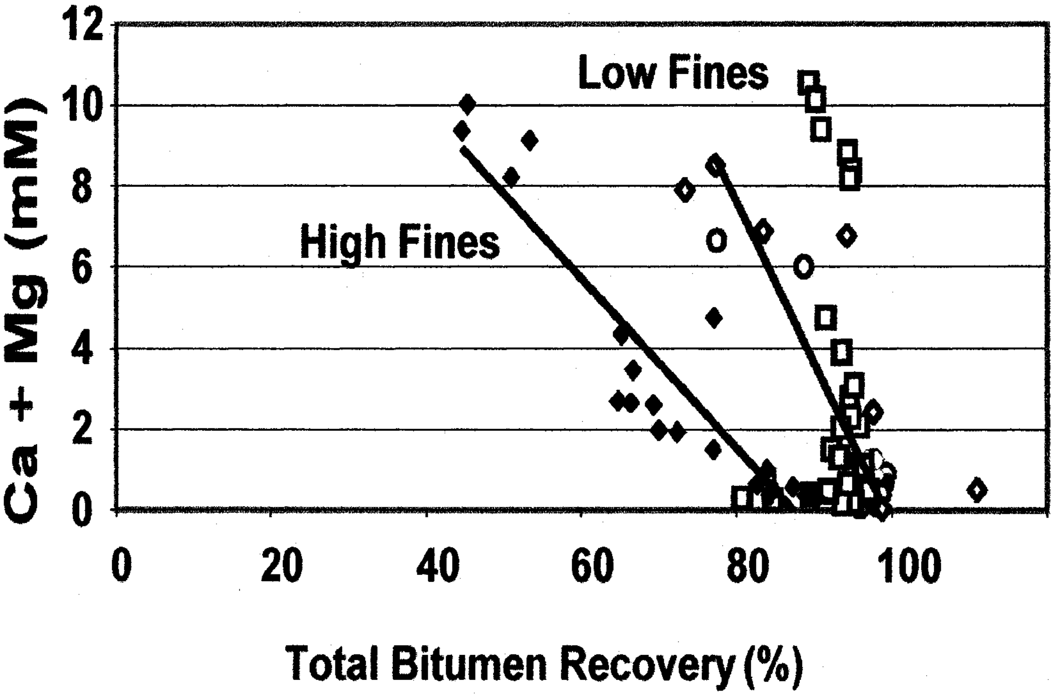


Figure 1-5: Effect of divalent ions on bitumen recovery for a low and high fine oil sands ores after Cuddy (2000)

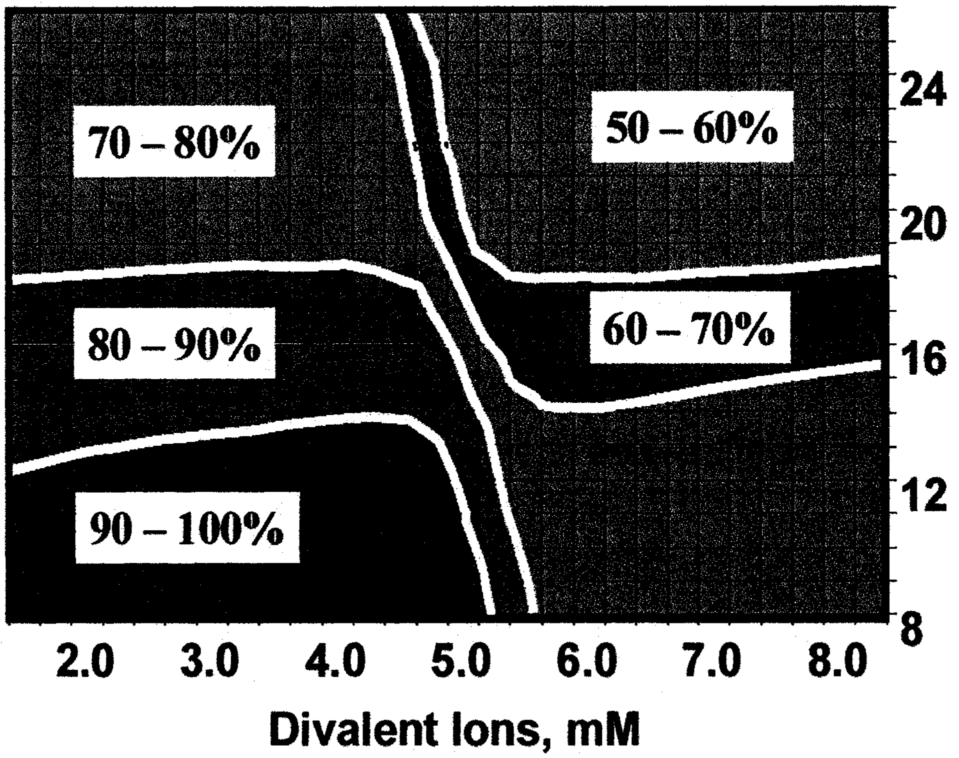


Figure 1.6: Map of bitumen recovery as affected by fines content and divalent ions after Wallace et al. (2001)

Figure 1-6 by Wallace (2001). This graph provides a rule of thumb to identify processing conditions and expected recoveries. The study suggests that to improve bitumen recovery to (90-100)% level, a good processing operation would consist of:

i) Reducing the fine solids content by blending ores and dilution of fines;

ii) Softening water by precipitating or by chelating dissolved divalent ions to lower their reactive concentration below 0.7 mM (Ca and Mg).

All studies considered fines without specifying clay type contents. Our study will use a novel doping test procedure to emphasize the depression of bitumen recovery by metal ions and different clay types that constitute the fines as they are found to be associated with poor processability of bitumen in commercial operations. Numerous studies recognized that fine clays and divalent calcium and magnesium ions in slurry contribute to the depression of bitumen recovery for good processing oil sands ores (Sanford and Seyer, 1979; Sanford, 1983; Smith and Schramm, 1992).

Among numerous factors identified, oxidation/ageing, metal ions in water and fine clays content in the ore were recognized as key variables that affect bitumen recovery. Because of the similarities in the hydrophobic characteristics of bitumen and bituminous coal, the depression effect of bituminous coal by fine clays and metal ions has been studied in our exploratory laboratory tests. Coal depression is attributed to slime coating of clays on coal surfaces. The slime coating is believed to result from the electrostatic attraction of negatively charged coal surface and the positively charged edges of typical clay particles, such as montmorillonite clay. In fact clay particles have dual electrical charge characteristics: negatively charged on the flat surfaces and positively charged on the edges (Van Olphen, 1977).

1.3 Objectives of this Research Work

The objective of the research undertaken in this thesis is to obtain a better understanding of the causes for poor processability of problem ores. This research aims at understanding the mechanisms that depress bitumen recovery during flotation of poorly processing ores. A new approach is developed to isolate operating variables that affect bitumen recovery during flotation and to identify bad actors that are responsible for depression of bitumen recovery and poor froth quality. By studying interactions among the identified key parameters, efforts are devoted to establishing a possible correlation between bitumen recovery and identified parameters, and to proposing strategies that minimize depression of bitumen flotation in processing problem ores. The innovative contribution of this research work is to study the processability of poor processing ores through modification of a good processing ore by doping bad actors until it behaves as a poor processing ore. More specifically, the good processing oil sands ore samples were doped with pure fine clays and processed with variable concentrations of metal ions. This novel approach allowed us to identify the role of various variables and their interactions in bitumen recovery. To better understand depression of bitumen recovery, a visual observation technique was developed to view the effects of changing variables on bitumen-air attachment and to study the effect of surfactants release on the size of air bubbles generated in process water.

1.4 Structure of the Thesis

Chapter 1 is an introduction to the entire thesis. It covers the general scope of the importance of oil sands in Alberta and it outlines the objectives of the thesis research aimed at understanding the nature of difficulties encountered when processing poor processing ores. We have described the hot water extraction process (HWEP) showing a process flow diagram of Syncrude Canada and the low energy extraction (LEE) process with a process flow diagram of Albian Sands. We have also recognized the slow progress made in understanding fundamental mechanisms of depression of bitumen recovery, and justified the need for further systematic study in this area. The novel approach of doping tests and using the visualization technique to isolate depressing factors and to identify their interactions that affect bitumen recovery are described.

Chapter 2 contains an extensive literature review on the status of research in oil sands ore processability. It covers such parameters as composition of the oil sands ores, contained surfactants, water chemistry and characteristics of fine clays that affect bitumen flotation. We have described core ore samples from Albian Sands and flotation fundamentals for the hot water extraction process (HWEP) and for the low energy extraction (LEE) process. Major findings and originality of the research with respect to poor processability of poor processing oil sands ores are summarized.

Chapter 3 describes the experimental details related to the current research. It covers the ore types tested, doping tests, experimental set up, visualization technique, experimental procedures for flotation tests and sample preparation for contact angles, surface tension and zeta potential measurements.

Chapter 4 represents the main body of the thesis, presenting the flotation results obtained to examine process variables such as Ca, Mg, MIBC (frother) and other additives, process temperatures and fines contents.

Chapter 5 presents the mechanistic study elucidating the role of fines and metal ions by contact angle, surface tension, zeta potential, induction time measurements and atomic force microscope.

Chapter 6 summarizes the accomplishment of this thesis research and provides some directions for the future work related to the use of polyacrylomide polymers as process aids for poor processing ores.

CHAPTER 2

LITERATURE REVIEW AND OVERVIEW OF BITUMEN EXTRACTION FUNDAMENTALS

"The oil sands industry is at cross road to develop viable strategies handling the problems associated with high fines and high multivalent cations using the knowledge derived from fundamental research of generations' efforts" (Masliyah, 2003).

Since the commercialization of the Clark hot water extraction process for bitumen recovery from oil sand ores, large amounts of research and development efforts have been focused on problem ores. The objectives of these efforts are to explain the depression mechanisms of bitumen recovery, to improve bitumen extraction from poor processing ores and to decrease production costs of bitumen to levels that are even lower than $ 12/Bbl that has been achieved at Syncrude Canada since 1999. Fundamental understanding and new conceptual models of bitumen recovery are now slowly emerging. However, the fundamentals of depressed bitumen recovery when processing problem ores remain to be established. The main challenges related to the poor processing ores include bitumen separation from fine sand grains, production of good quality froth, dealing with water management constraints, and handling tailings issues (George, 1998). The slow evolution is due to a myriad of chemical and physical interactions, and to a large number of variables involved in bitumen flotation as illustrated in Table 1-1. This literature review summarizes the current state of knowledge in understanding the fundamentals of the Athabasca oil sands extraction processes. It provides an overview on fundamentals related to this thesis for better understanding of research outcomes.

2.1 Composition of Oil Sands Ores

"Perhaps the single most characteristic feature of the Alberta oil sands, and almost certainly the most fortunate, is that the solid grains are water wet or hydrophilic. The oil in the pores is not in direct contact with mineral grains. Rather, each grain is surrounded by a thin film of water beyond which, in the center of the pore, is the oil. This hydrophilic tendency of the sands is fortunate because the hot water extraction process would not work if the grains were other than water wet" *(*Mossop, 1980).

Knowledge on the mineral composition of the Athabasca oil sands ores provides an important insight into the selection of flotation to extract bitumen from oil sands ores and into the origin of interaction between metal ions and clays that differentiate ore types and their behavior in processing.

2.1.1 Model Structure of the Oil Sand

The composition of the Athabasca oil sands consists of an intimate mixture of bitumen, water, sands, clays and other minerals. A model structure in Figure 2-1 shows that coarse sand grains are packed such that the voids occupy about 35% of the volume (Cottrell, 1963; Mossop, 1980). This packing around sand grains consists of a thin layer of connate water film that is about 10 nm thick (Takamura, 1982; Hall et al., 1983; Sparks, 2003). This connate water layer contains fine clays and encapsulates surfaces of individual sand

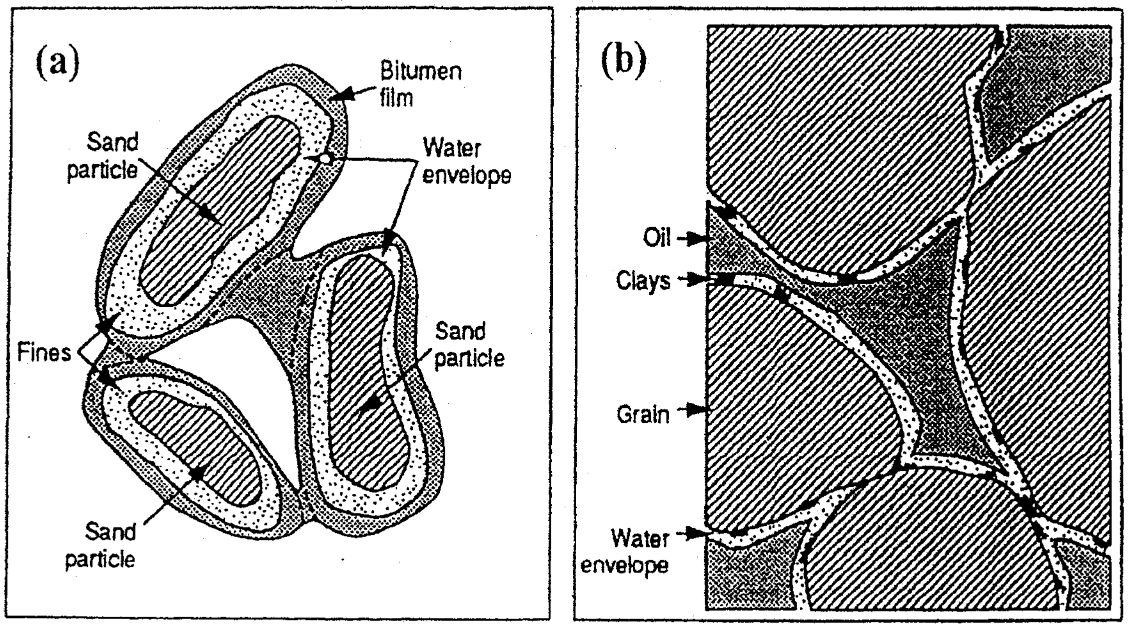


Figure 2-1: Schematic model structures of oil sand after (a) Cottrell (1963) and (b) Mossop (1980)

grains, which are believed to be hydrophilic (Clark and Pasternack, 1932; Bal, 1935; Clark, 1944; Fitzgerald, 1978).

Sparks et al. (2003) suggested that the hydrophilic properties of sand grains are due to insoluble matter that is physically and chemically adsorbed on solid surfaces and cause the surfaces to be water wet. The hydrophobic bitumen surrounds the connate water layer and fills the voids between the connate water encapsulating sand grains (Takamura, 1982). Viscous bitumen, mainly hydrocarbons with some natural surface active components, is naturally hydrophobic. These properties are essential conditions for successful application of water-based separation technology, illustrated in Figure 2-2, to separate hydrophobic bitumen from hydrophilic sand grains based on their difference in surface hydrophobicity.

Flotation is an economically attractive technology to recover bitumen from the Athabasca oil sands ores (Mossop, 1980; Masliyah, 2003). Bitumen is then recovered as an economic product. In general, the particle size distribution of solids is coarse with low fines content for high grade ores and fine with high fines content for lean ores. The oil sands deposits contain different mixtures of ore grades with variable processability by flotation when processed alone or blended. Such variations are encountered for ores from different mines and from one location to another within the same mine. An example of a cross section of an Albian Sands core sample is shown in Figure 2-3 and its characteristics are given in Table 2-1 (Paul, 2003).

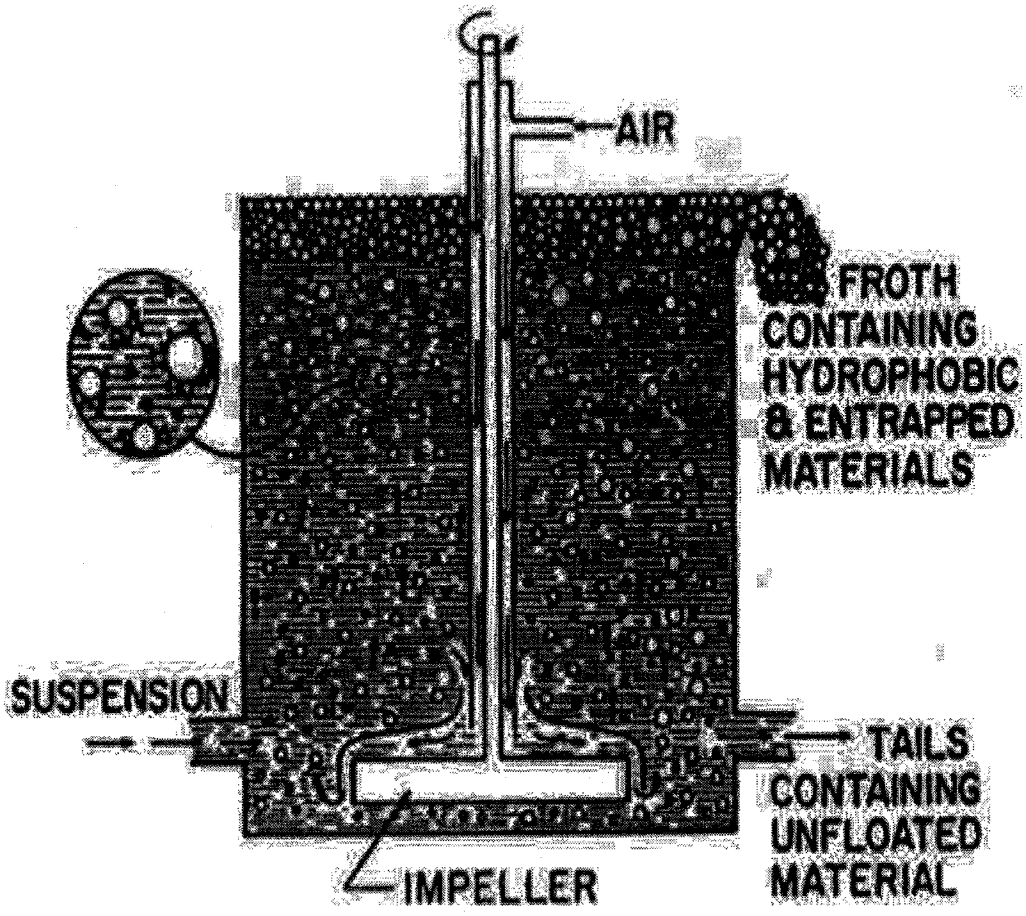
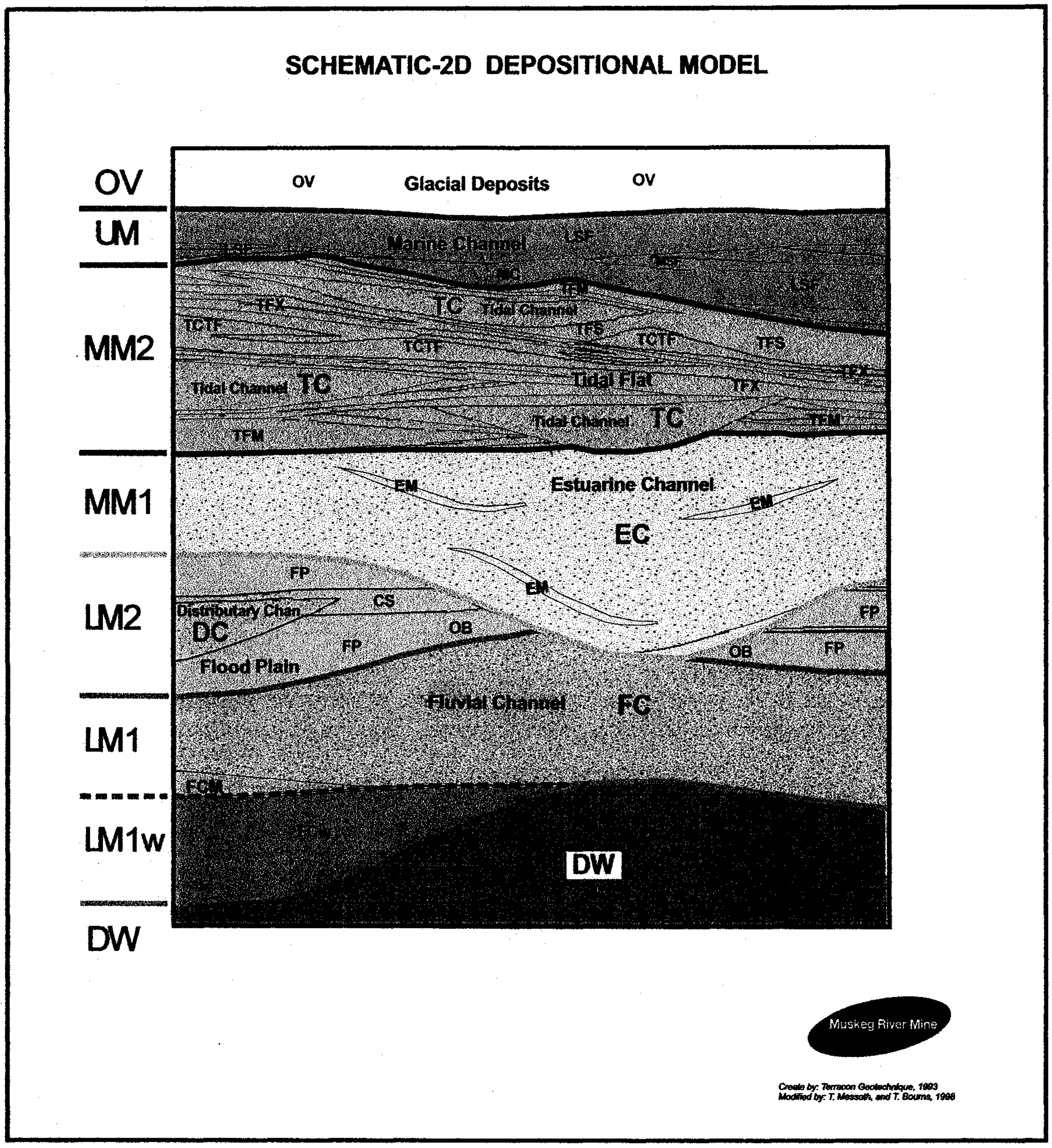


Figure 2-2: Basic principles of froth flotation


SCHEMATIC-2D DEPOSITIONAL MODEL

Create by: Terracon Geotechnique, 1993
Modified by: T. Massoth, and T. Bourns, 1998

Figure 2-3: Albian Sands mine model

Depositional Facies (Major Ore Facies Highlighted Yellow)				
			Facies	
		Member	Code	Name
		OV	OV	Overburden
Cretaceous - McMurray Formation	MARINE ENVIRONMEN	UM	OSM	Offshore Mud
			OST	Offshore Transition
			MC	"Marine Channel" Fill
			MB	Marine Breccia
			FS	Beach
			USF	Shoreface
			MSF	
			LSF	
			MLM	Marine Lagoonal Mud
	ESTUARINE ENVIRONMENT	MM2	SM	Salt Marsh
			MF	Mud Flat
			TFM	Tidal Flat Mud
			TFX	Tidal Flat Mixed
			TFS	Tidal Flat Sand
			TCTF	Tidal Channel/Tidal Flats
			TCM	Tidal Channel Margin
			TM	Tidal Channel Mud
			TC	Tidal Channel
			TCB	Tidal Channel Breccia
			TCw	Tidal Channel watersand
		MM1	ECT	Estuarine Channel Top
			ECM	Esturaine Channel Margin
			EM	Estuarine Channel Mud
			Ecf-Ecc	Estuarine Channel
			ECB	Estuarine Channel Breccia
			ECw	Estuarine Channel watersand
	CONTINENTAL ENVIRONMENT	LM2	BS	Back Swamp
			C0	Coal Swamp
			M	Marsh
			CS	Crevasse Splay
			DC	Distributary Channel
			FP	Flood Plain
			OB	Overbank
		LM1	FCT	Fluvial Channel Top
			FCM	Fluvial Channel Margin
			FM	Fluvial Channel Mud
			FCB	Fluvial Channel Breccia
			FCf-FCc	Fluvial Channel
			FFP	Fluvial Channel Floodplain
			CGL	Conglomerate
		LM1w	FCTw	Fluvial Channel Top (watersand)
			FCMw	Fluvial Channel Margin (watersand)
			FCBw	Fluvial Channel Breccia (watersand)
			FCw	Fluvial Channel (watersand)
			FMw	Fluvial Channel Mud (watersand)
			FFPw	Fluvial Channel Floodplain (watersand)
			CGLw	Conglomerate (watersand)
Devonian - Waterways	MARINE	DW	Psol	Paleosol
			Limy SH	Calcareous Shale
			Arg LS	Argillaceous Limestone
			Mic LS	Micritic Limestone
			Nod LS	Nodular Limestone
			Foss LS	Fossilliferrous Limestone

Table 2-1: Albian Sands Energy Inc., Muskeg River Mine Lease 13

2.1.2 Characterization of Fine Clays

In oil sands industry, mineral fines are defined as solids smaller than 44 microns. They are expressed as the percentage of total mineral content. The clay content of mineral fines is considered to contribute to the depression of bitumen recoveries (Sanford, 1983; Kasongo, 2000), to the increase of density and viscosity of middlings in the Primary Separation Cells (PSC), and to the increase of water content in the bitumen froths produced (Cuddy, 2000; Cox, 2000; Tipman, 2000). Clays are extremely small crystalline particles with diameters less than 2 μm. They are composed essentially of hydrous aluminum silicates. They appear in the ore in the form of a suspension in the connate water layer that surrounds coarse sand grains and as layers of variable thickness in the interbedded ore type formations as shown in Figure 2-3. In general, the majority of clays in the oil sands ores are kaolinite (22-76%), illite (7-10%), and (1-8%) montmorillonite. The typical chemical formula of these three types of clays is given by:

Kaolinite: $Al_4Si_4O_{10}(OH)_8$ (SG=2.61-2.68)
Illite: $K_{1-1.5}Al_4Si_{7-6.5}Al_{1-1.5}O_{20}(OH)_4$ (SG=2.6-2.9)
Montmorillonite: $(0.5Ca,Na)_{0.7}(Al,Mg,Fe)_4(Si,Al)_8O_{20}(OH)_4.nH_2O$ (SG=2.3).

Montmorillonite is a three-layer structural clay with pronounced swelling characteristics in water. Among the three types of clays, montmorillonite belongs to the smectite group of clays. It is the lightest with a specific gravity value of 2.3. It is referred to as an alumino-silicate in sequence of two tetrahedral (SiO_2) layers sandwiching one octahedral (AlO_6) layer. These three layer units are held together by sharing oxygen and hydroxyl groups between them and are electrically neutral. An important feature of montmorillonite is the isomorphic substitution of Si^{4+} by Al^{3+} in the tetrahedral layers and of Al^{3+} by Mg^{2+} in the octahedral layer. In both cases, atoms of higher positive valances (Si^{4+} and Al^{3+}) are substituted by those with lower valences (Al^{3+} and Mg^{2+}). This leads to a deficiency of positive charges, suggesting an excess of negative charges in the layers. The net interlayer charges are neutralized by interstitial K^+ or/and Na^+ counter ions. The negative charge resulting from the isomorphic substitutions will be confirmed in this study by the negative zeta potentials measured in aqueous solutions of operating pH range. When placed in water, the interstitial substitute ions are released, resulting in net negative interlayer charges. The strong electrostatic repulsion between layers causes interlayer to swell. Clay swelling is a significant factor in determining dewaterability and gelation of middlings (Rouquerol, 1999; Olphen, 1963; Kessick, 1978). Montmorillonite is more likely to build up as suspended solids in reclaimed water. Kaolinite is a two-layer structured clay with a small degree of isomorphic substitution. This structural characteristic makes kaolinite non-expandable in water. Illite belongs to a different class of three-layer structural clay that differs from montmorillonite by the absence of interlayer swelling in water. It should be noted that weathered illite could behave similarly to smectite montmorillonite in swelling and ion exchange capacity.

2.1.3 Water Chemistry

The raw water used to process oil sands in commercial plants is drawn from the Athabasca River. To ensure all the oil sands operations are under the zero discharge requirements, the river water is mixed in Albian Sands operations with tailings water reclaimed from the tailings ponds and with the thickener overflow water. Because of variations of ores and operating conditions, the ion concentration of water will change over time. As a result, the effects of water chemistry on depression of bitumen recovery will evolve with time. In general, higher ionic strengths lead to lower bitumen recovery and poorer froth quality for many ores. The composition of typical water from various sources is shown in Table 2-2 for Albian Sands. The metal ions best known for their negative impacts are calcium, magnesium, potassium, and sodium.

Table 2-2: Water chemistry for Albian Sands

Water source	**River water min-max (ppm)**	**Recycle water min-max (ppm)**
Conservative ions		
Na^+	9-48	18-98
K^+	1-3	1-11
Cl^-	3-47	17-85
SO_4^{2-}	4-53	19-77
HCO_3^-	84-220	95-383
Non conservative ions		
Ca^{2+}	20-54	26-65
Mg^{2+}	5-14	8-18

Although some of the dissolved inorganic ions come from the river water, they mainly originate from the ore itself, from process additives and from the recycle water. The composition of typical water from various sources is shown in Table 2-2 for Albian Sands. The dissolved ions are grouped into conservative and non conservative ions. The conservative ions are dissolved into water from the ore but they don't interact with oil sands species during processes. Such ions as Na^+, K^+, Cl^-, SO_4^{2-}, and HCO_3^- are considered conservative. The concentration of these ions builds up over time. The ore acts as a sink for the non-conservative ions, such as Ca^{2+} and Mg^{2+}. These ions interact with clays and bitumen such that they disappear either by precipitation or by adsorption on bitumen and/or solid surfaces. Some of the negative effects of high concentrations of non conservative ions can be corrected by using NaOH (Kasperski, 2001; Kasongo, 2000).

2.2 Hot Water and Low Energy Extraction Processes

The Athabasca oil sands extraction processes are reviewed here as individual sub-processes of recovering bitumen through conditioning and extraction stages. To better discuss the current state of knowledge on the fundamentals of bitumen recovery, the conditioning pertains to oil sand lump size reduction, ablation, bitumen liberation, and aeration. The extraction stages are discussed as results of attachment of bitumen to air bubbles, gravity separation, flotation and concentration of bitumen into froth.

2.2.1 Ore Conditioning

Similar to the processing of hard rock minerals, the objective of conditioning oil sand ores is size reduction, bitumen liberation, and aeration of liberated bitumen. The digestion is hereafter explained in steps, but it is more likely that they occur simultaneously in reality.

2.2.1.1 Size reduction

Oil sands ore is a non-consolidated material. Often, the oil sand ores are constituted of lumps stuck together by bitumen. When necessary, the first separation step consists of lump breaking using, for example, roller crushers before transportation of broken ore using belt conveyors.

2.2.1.2 Ablation

When oil sand ore lumps are mixed with hot water and are subjected to mechanical shear in tumblers, mixing boxes, rotary breakers or hydro-transport pipelines, their outer layer becomes heated, resulting in a reduction in bitumen viscosity. Once the oil sand lump becomes heated, its outer layer can be easily sheared away, which is known as ablation. As the surface bitumen is ablated, a fresh lump surface becomes exposed to the surrounding warm water and is heated again. This process repeats itself until the whole oil sand lump is ablated, producing slurries that contain sand grains that remain covered by a layer of bitumen.

2.2.1.3 Liberation

The temperature, applied mechanical agitation, interfacial properties and chemical additives collectively determine the liberation rate that takes place at the surface of sand grains. In the Clark hot water extraction process, the ablation, liberation and aeration are performed in tumblers. The slurry temperature is maintained at about 75°C-80°C with the addition of steam and hot water to decrease the viscosity of bitumen. A small amount of caustic is also added to maintain the pulp pH in the range of 8.0 - 8.5. In the low energy extraction (LEE) Process, the digestion is performed in rotary breakers and in slurry hydro transport pipelines with addition of warm water to maintain the slurry temperature at about 38^o- 40^oC as used in the Albian Sands Energy ore processing. There is no caustic addition in the LEE process. The ablated layers of hydrophobic bitumen on the surface of hydrophilic solid sand grains are under shear in water. Bitumen "liberation" from the surface of sand grain is illustrated in Figure 2.4 (Eskin, 2002; Masliyah, 2003; Masliyah, 2002). The liberation step consists of bitumen thinning that leads to pinning or the formation of a pinhole (I) that expands, and eventually leads to the recess of bitumen from sand grains into distinct growing bitumen droplets (II). It is suggested that the size of bitumen droplets depends on particle size distribution of sand grains. Bitumen droplets then detach from the surface of sand grains, becoming liberated under shear action in the digestion unit (III).

2.2.1.4 Aeration: Attachment and Loading of Bitumen on Air Bubbles.

The aeration of liberated bitumen droplets detached from the solid surface is done with air naturally present in the system or with injected air bubbles as shown in Figure 2.4b. Small bitumen droplets coalesce into larger ones (I) when they are on sand grains of wide particle size distribution. The larger bitumen droplets attach favorably to air bubbles (II). When formed from uniform and narrower particle size distributions, bitumen droplets would stay small and would poorly attach to air bubbles (III). In both cases, bitumen will

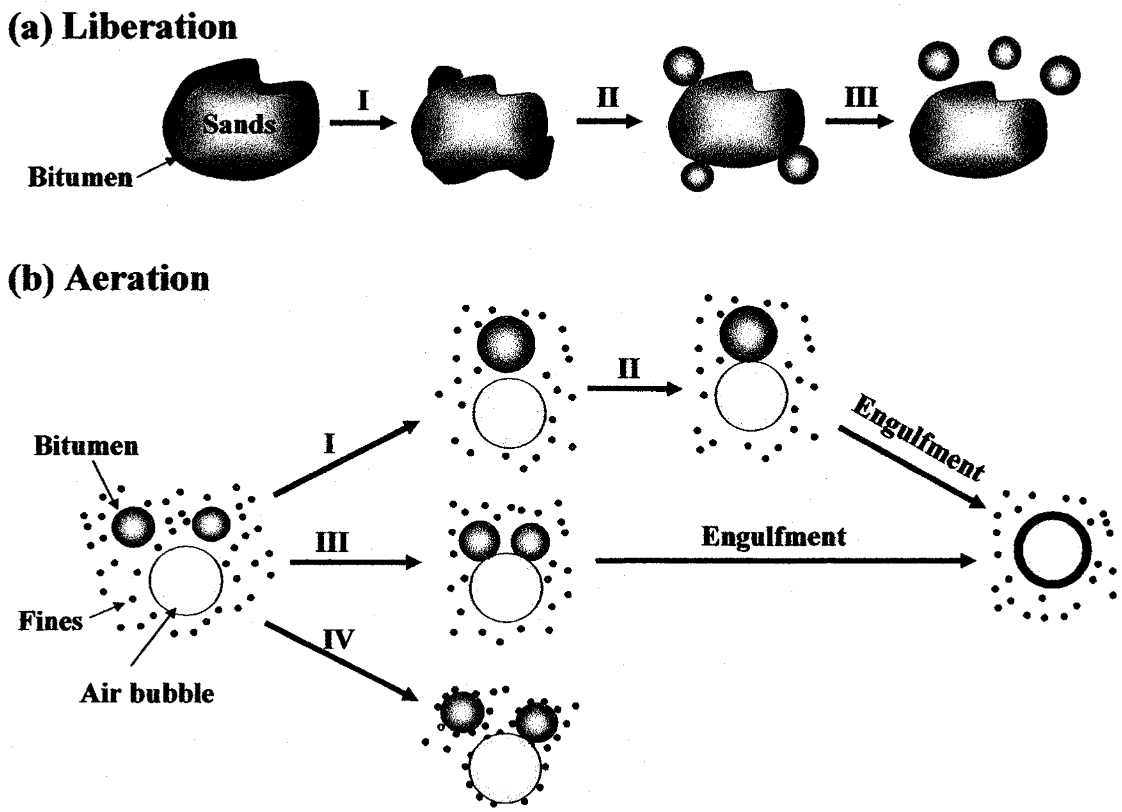


Figure 2-4: Conceptual stages for bitumen liberation and aeration after Masliyah (2003) and Liu (2003)

engulf the air bubbles upon attachment at high temperature; while at low temperature bitumen droplets will adhere to the air bubbles. The aerated bitumen-air aggregates rise through the slurry to the froth zone under the buoyancy force. Sufficient aeration is required to achieve the desired attachment (Clark, 1944; Clark, 1966). However, the aeration should not be excessive in order to avoid entrainment of minerals into the froth (Flynn et al., 2001; Clark, 1950; Camp, 1976).

Under good processing conditions, the fine clay particles that are water wet do not attach to the surface of bitumen droplets and they do not attach to the air bubbles in the system. They are dispersed by dilution water prior to gravity separation in primary separation cells (PSC) to prevent coagulation and any form of flocculation that may cause gelation of the pulp and unfavorably hinder the rise of bitumen-air aggregates, and hence bitumen loss to tailings (FTFC, 1995; Masliyah and Murray, 1999).

Coagulated fine particles may also become trapped into the rising bitumen droplets, resulting in poor froth quality. Under poor processing conditions, the hydrophilic fines will coat the surfaces of bitumen droplets and/or air bubbles, reducing their attachment (IV) and leading to low bitumen recovery and poor froth quality.

Different techniques were used to study aeration and air-bitumen attachment and to evaluate the loading of bitumen on flotation air bubbles (Malysa et al., Part 1and 2, 1999; Ng et al., 2000). In general, the diameter of bitumen loaded on a bubble in a bitumen-air aggregate is in the range of (0.2 – 1.2) mm and the mass of bitumen loaded is in the range of 10^{-6} g to 10^{-4} g, depending on the aggregate dimension (Clift et al., 1978; Masliyah et al., 1994, 1996). Ng et al, (2000) found that for different types of oil sand ores processed at 50°C with the same aeration rate, large air bubbles, with a bitumen-air aggregate diameter about 1 mm were generated for an estuarine good processing ore, leading to a load of (9×10^{-4}) g bitumen per bubble. However, for the poor processing marine ore, smaller bitumen-air aggregates with a diameter about 0.33 – 0.69 mm were generated (Zhou et al., 2000b). In this case, a lower bitumen load of (0.17 – 1.37) $\times 10^{-4}$ g per bubble is estimated. This lower bitumen loading on the air bubble is a direct consequence of weak attachment of bitumen to air bubbles for the poor processing ore.

2.2.1.5 Concentration of Bitumen in Froth

In the primary separation cells (PSC) the rising bitumen-air aggregates form a bitumen-rich primary froth that is collected at the top of the launder as the final extraction product. Fine clay particles and weakly hydrophobic bitumen droplets form the middling zone under the froth layer. They are withdrawn and processed in the scavenger flotation cells for further recovery of bitumen. At this stage conventional froth flotation cells or tailings oil recovery (TOR) vessels are used in commercial operations. Tails slurries from PSC and from scavenger cells contain minerals and residual amounts of fine bitumen droplets. The tailings slurries are collected for disposal in the tailings ponds. In the Albian Sands practice, the tailings are reprocessed through a secondary flotation stage. The froth from the secondary flotation stage is recycled to the primary separation cell, and the tails are classified with hydrocyclones. The cyclone underflow containing coarse minerals is used for construction to raise the dykes around the tailings ponds. The cyclone overflow is mixed with flocculent and transported to thickeners. The thickener underflow is disposed to the tailings pond beach. The warm water from the thickener overflow is recovered for heat and reused as dilution water in the primary separation cell.

2.3 Factors Affecting Hot Water Extraction Processes

2.3.1 Variables Affecting Bitumen Recovery during Flotation

2.3.1.1 Temperature

Bitumen recovery and froth quality depend on the strength of bitumen attachment to air bubbles, which is affected by different process variables such as process temperature and pulp pH. It has been observed that for operating temperatures over 50°C, as used in the Clark hot water extraction process (HWEP), decreasing temperature from 80°C to 50°C has only a small negative effect on bitumen-air attachment. Bitumen recovery decreases significantly below 35°C to such a degree that the operating plants may be forced to decrease the throughput in order to maintain recoveries, mostly for poor processing ores (Fitzgerald, 1978; Bichard, 1987). However, for the ores that contain a relatively large amount of fine solids, the increase in process temperature along with the change in physical parameters, such as aeration rate and agitation speed, may still not be sufficient to improve bitumen recovery and to produce bitumen froth of acceptable quality.

2.3.1.2 Slurry pH

The slurry pH has a significant impact on bitumen extraction (Basu, 1996, 1997a-b; 1998a-c). Increasing slurry pH by adding caustic (NaOH) is a convenient method to enhance the bitumen liberation from sand grains, to minimize bitumen-sand/clay coagulation and to improve bitumen recovery. Sodium hydroxide neutralizes organic acids present in bitumen. This enhances release of natural carboxylate surfactants $RCOO^-$ and sulphate SO_4^{2-}/sulfonate SO_3^- as polar groups (Bowman, 1967; Baptista, 1963, Sanford and Seyer, 1979). These surfactants are soluble in water where they are believed to help establish a bitumen/solid/water three-phase contact point, to initiate bitumen recession from the sand grains and to modify the electric surface potential of bitumen and fine solids. These effects of surfactants collectively result in easy separation of bitumen from solid sand grains and attachment of bitumen to air bubbles (Moschopedis, et al. 1977, 1980; Speight and Moschopedis, 1978; Ali, 1978; Schramm and Smith, 1985, 1987a-c; Smith and Schramm, 1992; Schramm, Smith, and Stone, 1984; Rowe et al., 2002; Starkweather et al., 1999, 2000; and Carroll, 1996). These authors mentioned the existence of a critical concentration of surfactants in water, which gives rise to maximum bitumen recoveries (Sanford, 1983; Cuddy, 2000; Wallace et al., 2001; Tipman, 2000). However, excessively high pH could result in excessive release of surfactants with risk of bitumen emulsification in the hot water extraction process (Dai and Chung, 1996).

2.3.1.3 Monovalent Metal Ions (Na^+, K^+)

Sodium (Na^+) and potassium (K^+) are conservative ions. They are dissolved in water from the ore and do not interact with oil sands species during bitumen extraction process. At pH 8.2, Basu (1996, 1997a,b; 1998a-c) showed that up to 16,000 ppm Na^+ is required to affect bitumen recovery. This concentration is higher than the conventional ionic concentration levels of about 1000 ppm. The effect of ionic strength on bitumen recovery was explained by the electrical double layer theory (Takamura and Wallace, 1987-88; Hepler and Smith, 1994; Basu, 1998b). Basu suggested that the loss of bitumen hydrophobicity due to high concentration of sodium ions could be restored with the addition of LEE (low energy extraction) chemicals as process aids. However, the LEE chemicals (kerosene and MIBC mixed at 2 to 1 volume ratio) are not used in any existing plant operations.

2.3.1.4 Divalent Metal Ions (Ca^{2+}, Mg^{2+})

The depressing effect of individual divalent ions, such as calcium (Ca^{2+}), magnesium (Mg^{2+}) and iron (Fe^{2+}) has been studied extensively (Clark, 1944; Speight and Moschopedis, 1977; Hepler and His, 1989; Smith and Schramm, 1992; Helper and Smith, 1994). These ions are non-conservative ions released in water from ores. They interact with various components during bitumen extraction process. In the tests of bitumen droplet recession from a glass slide, Basu (2000, 2003) showed that individual additions of calcium ion or montmorillonite clay affect both dynamic and static contact angles only marginally. Working with oil sands samples, Takamura and Chow (1983) observed a slow receding rate of a bitumen/liquid/solid three-phase contact line in the presence of calcium ions. Currie (1980) observed that in the presence of calcium ions (Ca^{2+}) the crumbling rate of the oil sand matrix was depressed and the ability of NaOH solution at pH 11.8 to cause crumbling was inhibited.

2.3.1.5 Fine Clays

The contribution of clays to the overall composition of oil sands ores is variable. Clays are considered to be responsible for some of the difficulties encountered with respect to recovery and froth quality (Baptista, 1989, Parts 1 and 2). The difficulty is, to a large extent, associated with the high specific surface areas of the fines. Baptista suggested that as the concentration of clays in the ore increases, the entrapment of bitumen and water inside clay structures increases, preventing such bitumen from being available for aeration. He suggested that the attachment of bitumen to air, its subsequent spreading around the air bubbles, and the recovery of bitumen are retarded in the presence of the exchangeable metal ions (Ca, Mg, Na, and K) that are released from clays. In fact, clay may interfere with bitumen coalescence and aeration. Clays can report to the froth zone by entrainment in water that is carried to the bitumen froth; by entrapment between bitumen droplets attaching to air bubble; by attachment to air bubbles due to modification of solid surfaces by adsorbed surfactants, and by slime coating on bitumen droplets (Baptista, and Bowman, 1969; Itokumbul, 1985; Shaw et al., 1994; Kotlyar et al., 1984, 1985, 1987, 1988; Chen et al., 1999; Zhou et al., 1998; Wang et al., 2003d).

2.3.1.6 Modeling Bitumen Recovery as a Function of Operating Conditions

In the commercial operations, statistics are used to study the effects of these operating variables on bitumen recovery by flotation. However, longer periods of time are needed to isolate any variable that is studied among numerous changing variables involved such as the ore characteristics and the operating conditions. Several authors have proposed mathematical models to simulate and describe the flotation process as a function of operating variables such as air flowrate, froth height and residence time (Lynch, 1981). These models were developed for sulfide ores. They are physically realistic, but remain imprecise when adapted to oil sands processing and describing bitumen recovery by flotation. A drawback of these models is that it is time-consuming to produce sufficient data for model development. Moreover the mathematics that is used is complex, hard to comprehend and not transparent to the operators. These limitations make the application of these models to oil sands plant operations rather limited. The development of oil sands extraction processes has evolved mostly because of bench scale laboratory work using testing techniques on representative ore samples. In the early stage of oil sands process development, jar tests were performed to determine conditions of bitumen separation from sand grains (Bichard, 1987). Syncrude developed a Batch Extraction Unit (BEU). Similar units were developed based on the Syncrude BEU concept. All the units were used with the purpose of evaluating bitumen recovery. The associated studies have been seen as a black box approach. To understand the mechanisms of bitumen flotation, the fundamentals of bitumen froth flotation, as summarized below, are required to interpret plant and laboratory results.

2.4 Fundamentals of Bitumen Froth Flotation and State of Knowledge

Flotation of bitumen results from aeration of bitumen during conditioning. The aeration results from collision and attachment between air bubbles and bitumen. The aggregates with an apparent density less than the density of pulp rise to the top of the pulp, forming a froth layer that overflows into the launder where bitumen froth is recovered with water and entrained solids. This process is complex, and a number of theories could be applicable to explain the separation processes. The ablation and liberation are governed by the electrokinetic and interfacial theories. Surface wettability and interactions between water, solid, air and bitumen control the aeration and attachment. The apparent density of the aggregates and the slurry viscosity determine the collection of air-bitumen aggregates into froth. A detailed review of these theories is beyond the scope of this thesis. However, to assist in the interpretation of our experimental findings and understanding the interactions between various components involved in the context of their effects on bitumen recovery, a brief review of the fundamentals of froth flotation is included. This section covers fundamentals on water chemistry, bitumen hydrophobicity, induction time, surface tension theory, adsorption of metal ions from solutions, surface charge of various components and atomic force microscopy.

2.4.1 Hydrophobicity and Concept of Contact Angle

Bitumen flotation is governed by its hydrophobicity. The extraction process relies on air as a carrier to transport hydrophobic bitumen from bulk slurries to the froth zone. Compressors are used to generate air bubbles by forcing air through capillary tubes and sparging it into slurries. Air bubbles are also generated by breaking compressed air into fine bubbles under shear forces provided by rotors of agitators and by spargers. The rotors disperse air throughout the slurry in flotation cells.

The extraction process involves the selective attachment of air bubbles to bitumen droplets, forming aggregates that rise from the bulk of slurries, to the froth zone. The efficiency and stability of the attachment are determined mainly by the degree of surface hydrophobicity that is measured by the contact angle. Figure 2-5 shows an air bubble that is attached to a bitumen surface in water.

The contact angle (θ) is measured through the water phase at the three phase contact point X using procedures described in the next chapter. Three forces determine the magnitude of the contact angle: the surface tensions at the air-bitumen (σ_{ab}) and air-water (σ_{aw}) interface and the interfacial tension at bitumen-water interface (σ_{bw}).

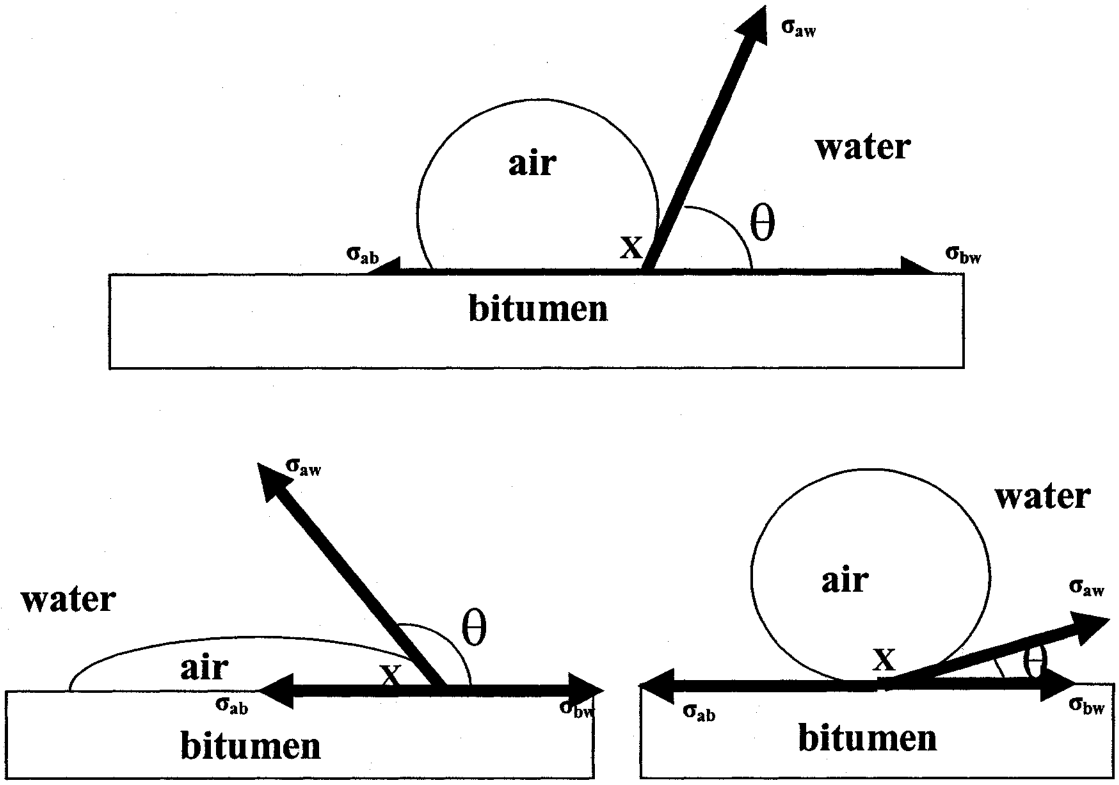
Under ideal static conditions, the surface of bitumen could be considered macroscopically smooth, rigid, homogeneous, and chemically and physically inert with respect to the surrounding water. At the equilibrium among the three interfacial tensions at the three phase contact point, the air bubble would stand on the surface of bitumen, leading to a unique static contact angle. The value of contact angle is given by following force balance:

$$\sigma_{ab} = \sigma_{bw} + \sigma_{aw} \cdot \cos\theta \tag{2-1}$$

where θ is the equilibrium contact angle. The above force balance equation can be rearranged to become the well known Dupre-Young's equation:

$$Cos\ \theta = \frac{\sigma_{ab} - \sigma_{bw}}{\sigma_{aw}} \tag{2-2}$$

This equation suggests that an increase in the contact angle θ, or a decrease of $\cos\theta$ could result from an increase of the surface tension of water σ_{aw}, and/or a decrease of the surface tension of bitumen σ_{ab}, that has to be larger than the decrease in water-bitumen



More hydrophobic
(easy to float)

Less hydrophobic
(difficult to float)

Figure 2-5: Concept of contact angle

interfacial tension σ_{bw} (Klassen and Mokrousov, 1963). Therefore, any changes in a process that causes changes in any of three surface or interfacial tensions would cause a change in contact angle and hence in floatability.

Under commercial conditions, systems are dynamic. The bitumen surface is often not smooth, not rigid and heterogeneous. Moreover it may react with the process water that is not chemically and physically inert. The unbalance of the three surface/interfacial forces is then expressed by:

Either $\sigma_{ab} > \sigma_{bw} + \sigma_{aw}$ (spreading) (2-3)

when water advances and spreads on bitumen surface. This leads to a poor air-bitumen contact in water.

Or $\sigma_{ab} < \sigma_{bw} + \sigma_{aw}$ (2-4)

when water recedes from the bitumen surface. This leads to a good air-bitumen contact in water, and the water reaches a point to establish contact angle.

There is a difference between the advancing contact angle θ_a at the advancing edge, and the receding contact angle θ_r at the receding edge of the liquid drop. This difference is known as the contact angle hysteresis:

$$\theta_{hysteresis} = \theta_a - \theta_r \quad (2\text{-}5)$$

In mixing slurries, air bubbles impinge bitumen surfaces by forcing water to recede. We consider the receding contact angle to be a more suitable measure of dynamic hydrophobicity as it reflects flotation process of bubble attaching to bitumen. Techniques used to measure contact angle θ are inspired from Young's equation, and they usually consist of a goniometer and a captive air bubble that is generated at the tip of a micro syringe and pressed against a spin-coated bitumen surface in water.

2.4.2 Induction Time

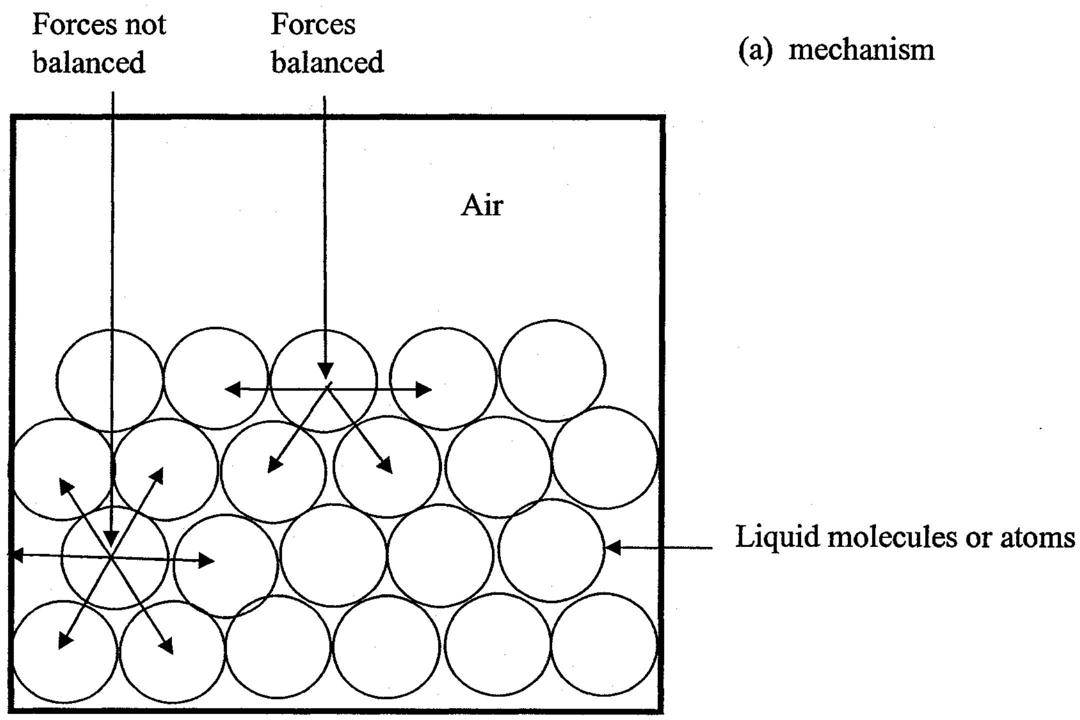
The induction time is the minimal time, in microseconds, that is required to make contact between an air bubble and bitumen surface and induce attachment. This time includes periods for thinning the disjoining liquid film between the air bubble and bitumen droplet to a critical thickness. It includes the time for breaking the water film, and for expanding the three phase contact point to form a stable attachment that can withstand the inertia force of detachment during mixing and rising of aggregates to the froth zone (Wang, 2003; Gu, 2003). The induction time is shorter for an hydrophobic surface than for an hydrophilic surface where the disjoining film is persistent, and constitutes a barrier for attachment to take place (Fersteneau, 1976). In this last case, the attachment is weaker and the recovery would be poorer. The induction time is measured by bitumen "pick-up" tests which measure the time required to induce attachment by pushing an air bubble against a bitumen surface, and then lifting the bubble to examine whether the bubble becomes attached to the surface. The results showed a shorter induction time for smaller air bubbles, indicating that small bubbles attach relatively easily to bitumen surface and are favorable for bitumen flotation.

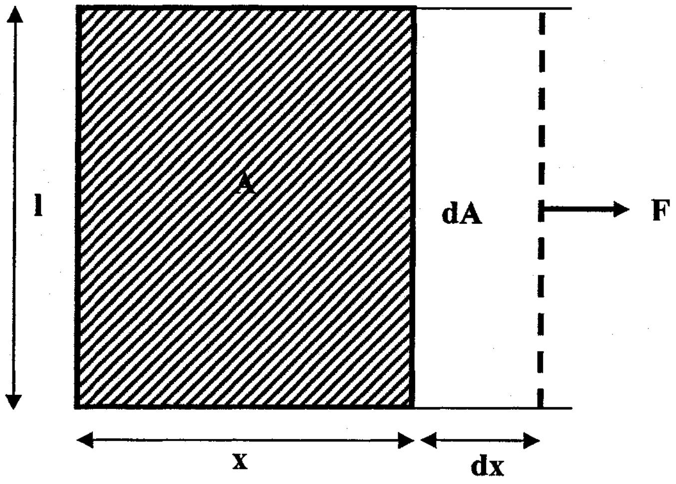
2.4.3 Surface Tension of Supernatants

During the extraction of bitumen, natural surfactants are released from the ore to the process water. The released surfactants modify the surface tension of water (Shaw, 1999; Osipow, 1962). Lowering the surface tension at the liquid-air interface enhances bitumen flotation due to generation of finer air bubbles. To illustrate the concept of surface tension, let us consider the inside of a bulk liquid, where molecules and atoms are completely surrounded by other molecules or atoms, as shown in Figure 2-6a. They interact with balanced forces in all directions. The energy to move molecules inside the bulk phase is small. The molecules at the surfaces differs from the interior molecules of the phase as the number of nearest neighboring molecules is reduced by the lack of neighboring molecules on surface. In this case, attractive inter-molecular forces are no longer equalized around molecules on the surface. The force is only from one side, and is directed inward towards the bulk.

To move a molecule from the interior phase of a fluid to the surface, more energy is required to balance the unbalanced forces. The surface tension corresponds then to the energy required to hold the molecules on the surface or to extend the surface to overcome these forces. A film of detergent in water illustrates this concept by forming an area "A" in a wire frame, "l" long and "x" wide. One side of the frame is movable, as illustrated in Figure 2-6b. To expand the surface area A by area dA, a work dw is exerted by applying

(a) mechanism





(b) Work $= F\,dx$ (2-6)

$= \sigma\,dA$ (2-7)

Figure 2-6: Concept of surface tension

a force F to the movable side and moving it by the distance dx. The expanded area on the two faces equals to dA, and the work dw is expressed by:

$$dw = F\,dx \tag{2-8}$$

$$dw = \sigma\,dA \tag{2-9}$$

$$dA = 2\,l\,dx \tag{2-10}$$

where dA is the new stretched surface area, and σ is the surface tension or energy per unit area in $mJ/\,m^2$ that is required to create new surfaces. It is also expressed as:

$$\sigma = \frac{F}{2l} \tag{2-11}$$

$$l = 2\,\pi\,R \tag{2-12}$$

where l is the length of a ring of radius R that is used for measurements.

2.4.4 Adsorption of Metal Ions from Solutions

Adsorption is any process whereby molecules or ions or atoms adhere to a surface of a liquid or a solid. Adsorption may lead to changes in surface charge characteristics. In fact, forces are unbalanced and any molecule or atom at the surface has the power to attract any external neighboring molecules or foreign ions that comes within their sphere of influence.

2.4.5 Surface Charge and Zeta Potential of Suspended Particles

The adsorption phenomenon at a bitumen/water interface is controlled, in most cases, by surface charge that has a profound effect on testing individual components in water. The surface charge of bitumen could be modified to enhance coalescence of bitumen droplets. Such a change could be beneficial to bitumen flotation. The surface charge of clays can also be modified to enhance flocculation of fine clay particles. Slime coating of fine clays on bitumen surfaces caused by changing the surface charge is detrimental to bitumen flotation because the slime coating on bitumen builds up hydrophilic barriers that prevent direct contact of air bubbles with the hydrophobic bitumen surface. This slime coating causes a reduction in bitumen recovery and it leads to poor froth quality. The effect of slime coating on mineral flotation is well documented by Fuerstenau (1985); Takamura and Wallace (1988); and Takamura and Schramm et al. (1985). The slime coating effect was initially believed to result from electrostatic attraction between clays and bitumen (Bichard, 1987). Bowman (1967) adopted the concept of surface charges on a bitumen/water interface to explain the bitumen/water/solid/air interactions in a Hot Water Extraction system. Takamura and Chow (1985, 1986) adopted the surface ionization model (Healy and White, 1978) to bitumen systems to understand the electrical properties of a bitumen/water interface (Masliyah, 1994). They assumed that the charge at the bitumen/water interface is derived from the dissociation of carboxylic groups. The effect of pH and calcium ions on bitumen displacement from a sand grain surface could be reasonably explained by their model (Takamura and Chow, 1983; Currie et al., 1980).

2.4.6. The Electric Double Layer

Mineral particles in an aqueous suspension almost invariably carry a surface charge that is generally negative, except in a few instances where the pH is very low. This surface charge may be acquired by unequal dissolution of ions from the mineral, by surface ionization, or by preferential adsorption of anions or cations. Minerals become positively charged at acidic pH, and negatively charged at alkaline pH, with the point-of-zero charge (PZC) or isoelectric point at an intermediate pH. The isomorphous substitutions in the mineral lattice and the dipole orientation are two other ways of surface charge acquisition. Because of the surface charge, ions of opposite charge in solution will be attracted towards the surface as shown in Figure 2-7. The counter-ions are held to the surface of the particle by electrostatic attraction. There will therefore be a higher concentration of counter-ions close to the surface than in the bulk of the liquid. This concentration falls off with increasing distance from the surface of the particle. The first layer is a compact layer of counter-ions that are strongly attached to the surface, which is called the inner bound Stern layer. This rigid layer makes direct measurement of the surface charge of the particles impossible. This layer moves with the surface when the particle moves with respect to its medium. Next to the Stern layer is a layer where the counter-ions are distributed according to a balance between their diffusion and the forces of electrostatic attraction. This outer region is called the Gouy-Chapman diffuse layer. This layer is not carried with the surface when the particle moves with respect to its

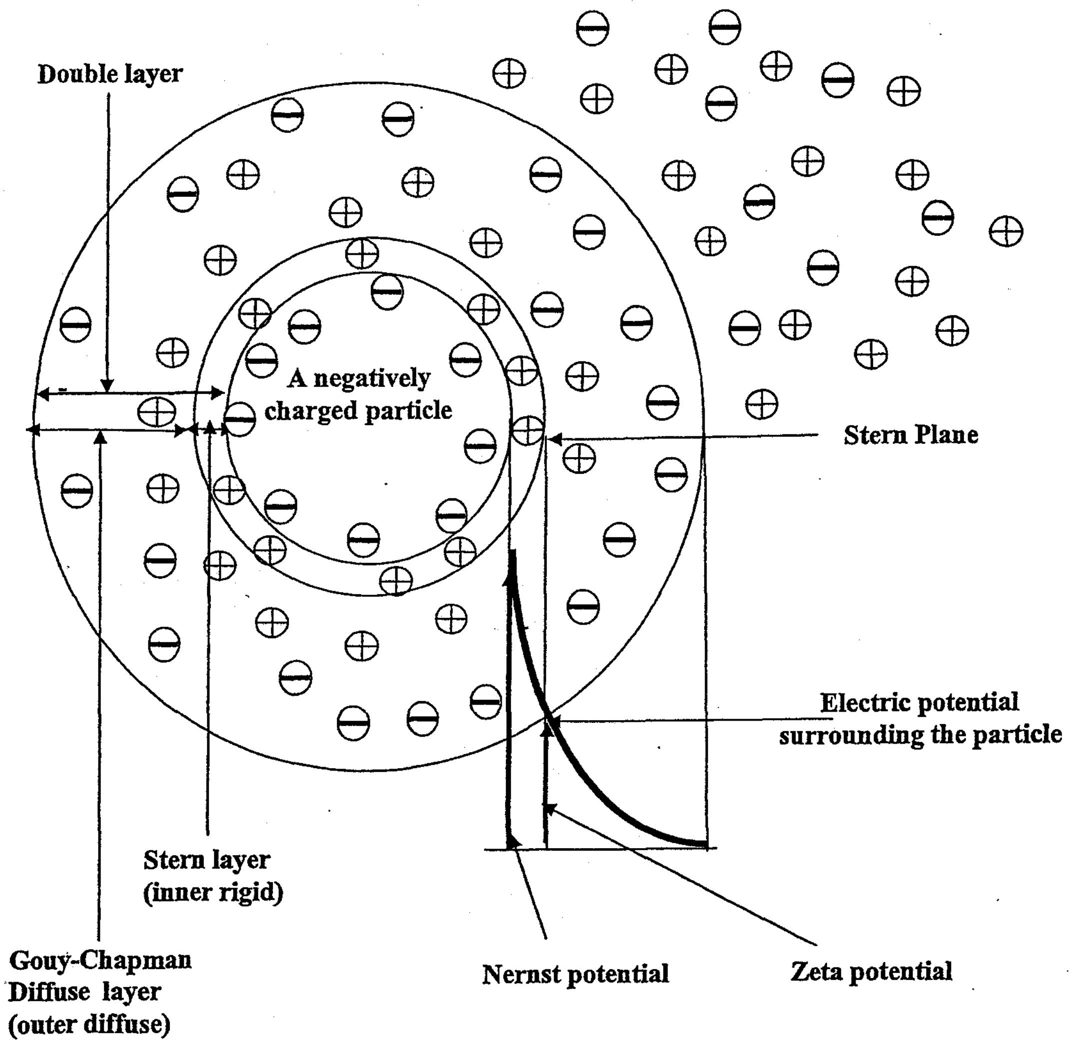


Figure 2-7: Concept of zeta potential

medium. The two layers, the inner bound layer and outer diffuse layer, form the electric double layer. The shear plane separates them, and the potential at the shear plane, outside the Stern layer, is conventionally defined as zeta potential (ζ). It is referred to as the potential at the slip plane between the fixed and the flowing liquid. The actual surface potential cannot be measured, so the potential at the shear plane is considered to be its best estimate because it can be determined more easily than the actual surface potential. The potential drops to zero in the bulk of the solution into which ions are randomly distributed. Electrokinetic phenomena are only directly related to the nature of the mobile part of the electric double layer and may, therefore, only be interpreted in terms of the potential or the charge density at the surface of shear plane.

Zeta potential (ζ) is commonly measured using an electrophoresis technique. In this technique, an electric field E (volts/meter) is applied to charged particles suspended in a supporting electrolyte solution. It acts on the double layer of the particles and forces them to move at a constant velocity υ (meter/sec) with respect to the electrolyte in the stationary plane. The electrophoretic mobility (υ/E) is expressed as the ratio of the velocity υ to the applied electric field E. Zeta potential (ζ) is related to the electrophoretic mobility (υ/E) by the simplified Helmholz-Smoluchowski equation (Van Olphen, 1963 and Masliyah, 1994):

$$\zeta = \frac{3}{2}\frac{\eta}{\varepsilon\varepsilon_o}\frac{\upsilon}{E} \qquad (2\text{-}13)$$

where η is the viscosity of the fluid, ε_o the permittivity of vacuum (C/V.m) and ε is the dielectric constant.

To explain the depression of bitumen recovery, Bowman (1967); Takamura and Chow (1983); Takamura and Wallace (1988); and Zhou et al. (1999) suggested that the attraction between solids and bitumen droplets was due to the adsorption of calcium ions that alter the electrical double layers. They suggested that the formation of calcium carboxylic complexes played a role in bridging bitumen and solids, thereby retarding bitumen recovery and affecting bitumen froth quality.

2.4.7 Atomic Force Microscopy

Atomic force microscopy (AFM) can be used to measure the interactive forces between bitumen and clays in water. The description of the measurement procedures and principles of the colloidal force measurement using AFM technique are outlined in appendix 1 and in literature (Ducker et al., 1991, 1992; Rabinovich et al., 1994; Kappl and Butt, 2002). AFM allows for determination of colloidal forces between two surfaces at long range by the deflection of a cantilever when the probe is not in contact with the surface. The adhesion force is measured as the force required to separate the probe particle from the surface. Liu (2003) confirmed that a higher adhesion force would suggest a stronger coagulation between bitumen and clays; indicating that bitumen cannot be separated from clay particles even under extensive mixing conditions. In the presence of calcium ions, a stronger adhesion force was measured between bitumen and montmorillonite clays. In contrast, in the absence of calcium ions, a highly repulsive force was measured, indicating the absence of coagulation between bitumen and clays. This finding confirms the findings of the contact angle measurements, that montmorillonite clay particles can easily approach a bitumen surface in the presence of calcium.

2.5 Summary

Conditioning encompasses ore preparation stages during which the ore lumps are broken down mechanically in water with the use of crushers, tumblers, or breakers. Liberation takes place when bitumen is stripped off sand grain surfaces. The detached bitumen forms small droplets that are dispersed in the slurry by mixing. Since bitumen droplets have densities similar to water, effective separation of them from pulp requires aeration. The air-bitumen aggregates rise through the slurry to the top of the pulp where bitumen froth is collected. Many factors affect the processability of oil sands ores but the depression mechanisms of bitumen recovery remain poorly understood.

Diverse theories to explain the depression of bitumen recoveries were reviewed. The increase of calcium ion concentration decreases the maximum repulsive force barrier that needs to be overcome to initiate coagulation between bitumen and clays. Atomic force microscopy (AFM) directly measures repulsive forces using the deflection of a cantilever when a probe clay particle approaches a bitumen surface in an aqueous solution. AFM measurements have shown that calcium ions might act as a bridge by adsorbing on both the montmorillonite clay and bitumen surface. The results indicate that calcium addition can depress the repulsive force barrier, and enhance the adhesion between bitumen and montmorillonite clay particles. The resulting slime coating of montmorillonite clay particles on bitumen surfaces creates a steric barrier on the bitumen surface and renders it less hydrophobic. This slime coating will lead to poor air-bitumen attachment and hence poor bitumen recovery. The results from the zeta potential distribution measurements and AFM studies confirm the negative impact of montmorillonite clays on bitumen recovery in the presence of calcium ions.

CHAPTER 3

MATERIALS AND EXPERIMENTAL PROCEDURES

The doping test is an innovation that we add to the BEU procedure to study bitumen flotation at the bench scale. This approach allows isolation of one or more variables for investigation during flotation. It allows evaluation of their effects on bitumen recovery, froth quality, and quality of tailings produced. The interpretation of results from doping tests is facilitated by the visualization technique that we have developed in this study. Visualization allows visual observation of events in slurries. It is a promising method for qualitatively assessing the effects of changing operating variables on process performance. It allows visual confirmation of the results that empirical and theoretical models would intend to describe. The results obtained with the combination of doping test and visualization shed light on bitumen flotation process.

3.1 Preparation of Ore Samples and Experimental Setup

The bulk raw ore samples were received from Syncrude Mildred Lake North Mine, from Aurora mine and from Albian Sands Energy Inc. Muskeg River Mine. All these mines are located near Fort McMurray. The composition of ore samples used for this research work is given in Table 3-1. They represent a variety of poor and good oil sand ores, characterized by their bitumen content, water content, and solid content and mining locations. Our conclusions are valid for the oil sand ores sampled. The approach can be extended to ores with characteristics that differ from the ores studied.

Table 3.1: Composition of oil sands ore samples studied

Ore type	Mining location	% Bitumen	% Water	% Solid
Good Ore	Mildred North A	10.66	7.12	82.22
Good Ore	Mildred North G52-55	10.52		
Good Ore	Mildred North 58-67A	10.74	4.66	84.6
Good Ore	Mildred North 77-81A	10.35		
Good Ore	Mildred North 91-149	13.91		
Good Ore	Mildred North 186-223	14.88	0.89	84.01
Good Ore	Mildred North 152-158	13.5	2.58	83.7
Good Ore	Mildred North 161-173	14.62	0.87	84.58
Good Ore	Mildred North 174-180	12.47	1.06	83.16
Good Ore ASE	Muskeg River Mine 181-183	13.87	0.73	84.2
Good Ore	Mildred North 119-121			
Moderate Ore	G39-42	9.34	5.65	85.02
Lean Ore	Mildred North	6.15		
Lean Ore	Mildred North 63	7.79	11.85	80.37
Lean Ore	Mildred North 68-75, 88-90 B	7.83		
Lean Ore	Mildred North 225-236	6.05	7.1	86.85
Lean Ore	Mildred North 150-172	7.15	6.36	86.4
Lean Ore	Mildred North 160-65	7.4		
Transition Ore	Aurora Mine 237-238	9.44	7.12	83.44
Oxidized Ore	239-240	12.15	0.71	87.14

To obtain representative subsamples, the bulk samples were chopped with a Comil mill to reduce the particle size of the feed sample and to permit homogenization and subsampling (Wallace, 1981 and 1985; Shaw, 1981). All noticeable rocks, siltstones, and solid clay lumps were removed manually. The samples were rolled and mixed on a tarp using coning and quartering techniques for preparation, splitting, scooping and packing of samples into 600-g plastic bags. The packed samples were stored in a freezer at – 29°C to minimize weathering. All the tests were carried out at natural pH that was measured but not controlled.

The batch flotation tests were performed to mimic the commercial Clark Hot Water Extraction Process, and to study the effect of such process variables as water chemistry and ore characteristics on bitumen recovery and froth quality. The batch tests were conducted in a modified laboratory Denver flotation cell shown in Figures 3-1 and 3-2. The volume of the cell is 1.5-liters. The cell is modified to have a 1-cm thick water-jacket that is connected to a Neslab RTE-111 thermal bath to maintain circulation of warm water, to provide heat, and to control the slurry temperature. The unit was used to study the depression mechanisms of bitumen recovery by poisoning naturally good processing ore samples with controlled modifications of water chemistry and clay addition.

All clay samples used were ordered from Wards' Minerals. Kaolinite and illite clays received required a certain degree of ore processing to break any wide range sizes that always naturally remain in the samples by dry pulverizing and screening in preparation for use in the lab sizing under 4 microns (Wards' Minerals). They are characterized in

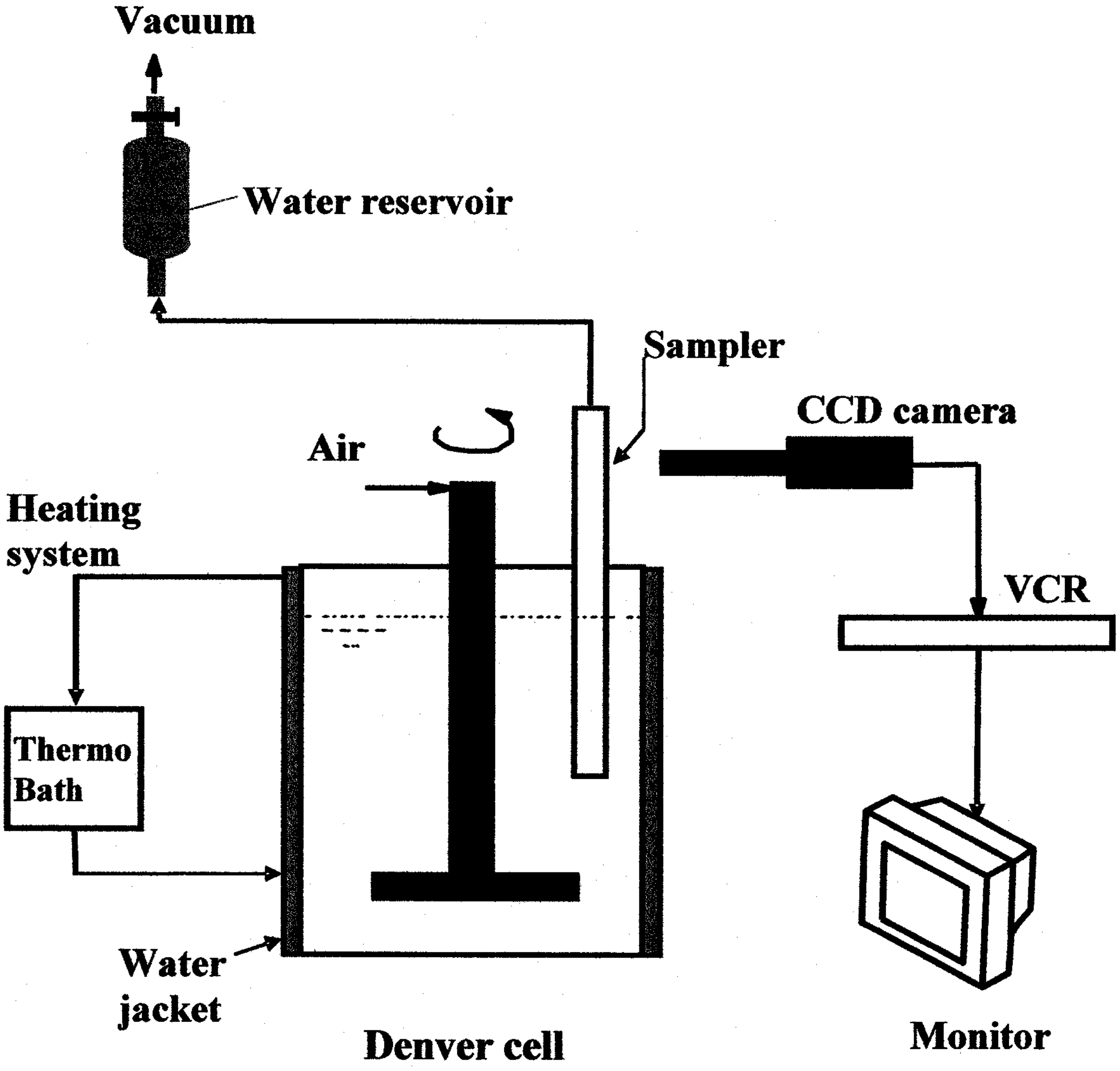


Figure 3-1: Laboratory experimental setup

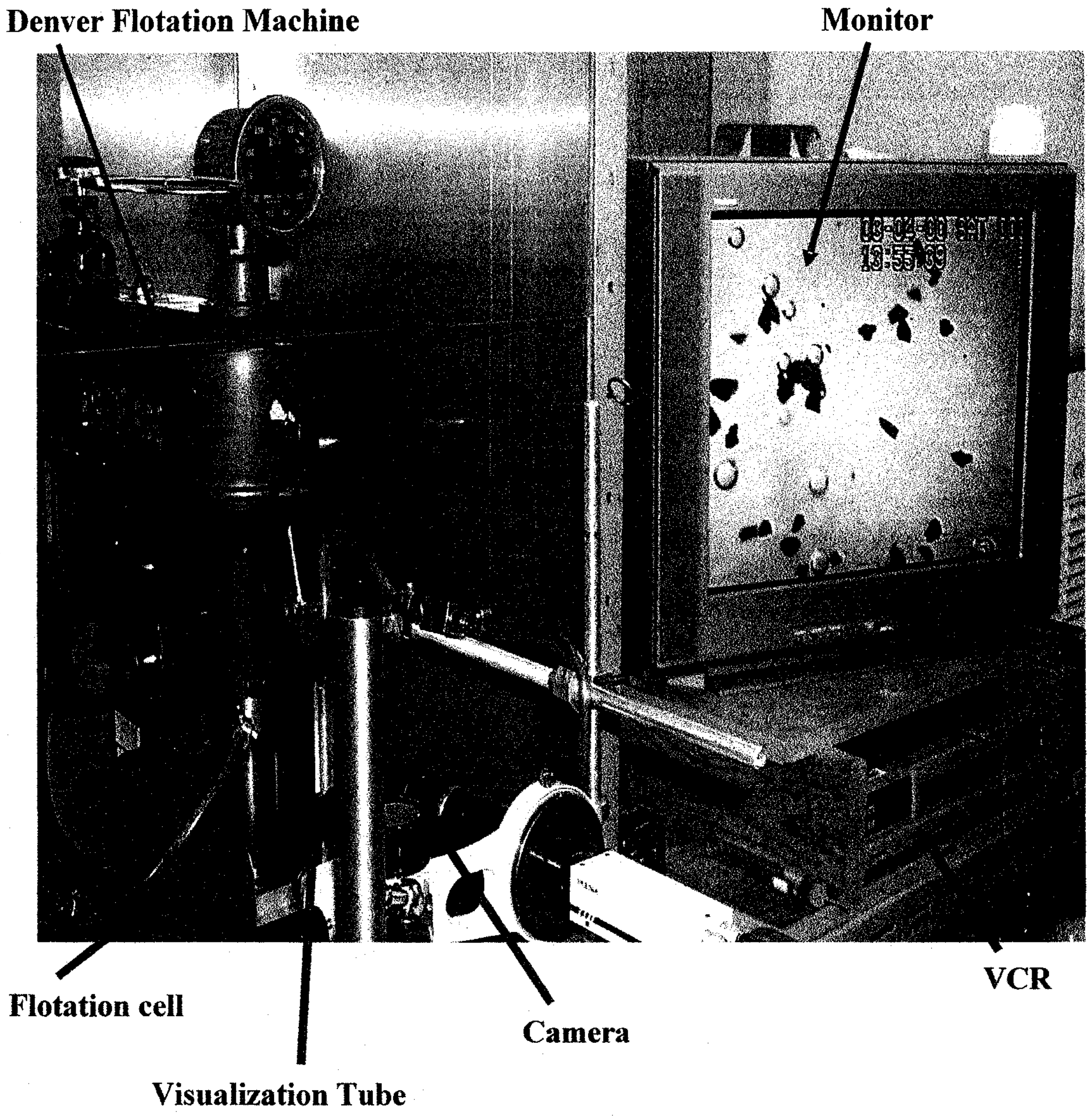


Figure 3-2: Photography of the laboratory experimental setup visualizing the attachment of coal during flotation

Table 3.2 that shows that Montmorillonite is lighter than kaolinite and illite clays with a specific gravity of 2.3. It provides more external surface area at 40-100 m^2/g of clay and as high as 800 m^2/g when the external and the internal surfaces are considered accessible to exchange ions in the water (Olphen, 1963). The cation exchange capacity (CEC) that expresses the total amount of ions that are exchangeable with available cations in water ranges high at 80-100 meq per 100 g of dry montmorillonite, medium at 20-40 meq per 100 g of dry illite and low at 1-10 meq per 100 g of dry kaolinite. The density of charge derived from the cation exchange capacity and the surface area per gram of clay is in the order of 10 $\mu C/cm^2$ for montmorillonite and they are lower for illite and kaolinite if we consider only the cations located on the exterior surfaces.

Table 3.2: Characteristics of clay minerals

Clay types	**Specific gravity**	**Surface area**	**CEC**	**Charge density**
		m^2/g	meq /100 gr	uC/cm^2
Kaolinite	2.61- 2.68	10 - 30	1 - 10	-
Illite	2.6 - 2.9	-	20 - 40	-
Montmorillonite	2.3	40 - 100	80 - 100	10

The deionized water used throughout was prepared with an Elix 5 followed by a Millipore ultra water purification system. Calcium ions were obtained from chloride hexa hydrate salt $CaCl_2.6H_2O$ that has high solubility in cold and in hot water.

Bitumen flotation from poor processing ores is characterized by weak attachment of bitumen to air bubbles. This results in bitumen primary recovery that is lower than 70% as shown in Figures 1-5 and 1-6. Bitumen recoveries from poor processing ores are less sensitive to changes in the operating variables. It is therefore extremely difficult to understand the depression mechanisms of bitumen recovery from poor processing ore samples. Bitumen recoveries from good processing ores are found to be more sensitive to changes in additives. The novelty of this study consists of identifying variables and determining their critical conditions that result in poor processability of ores by poisoning good processing ore with additives such as metal ions and clays to make the ore behave like a poor processing ore. This approach allows the effect of changing additives and operating conditions on bitumen recovery and froth quality to be determined. The results of the tests with doping additives are compared with those from baseline flotation tests using good processing ores without additives. They are also compared with previous findings from plant operations and from literature. For simplicity of result interpretation, all known variables such as slurry density, slurry temperature, conditioning time, agitation intensity, and aeration rate were kept constant in our tests. The procedure of the bench scale flotation experiments is given in Figure 3-3 and is described below.

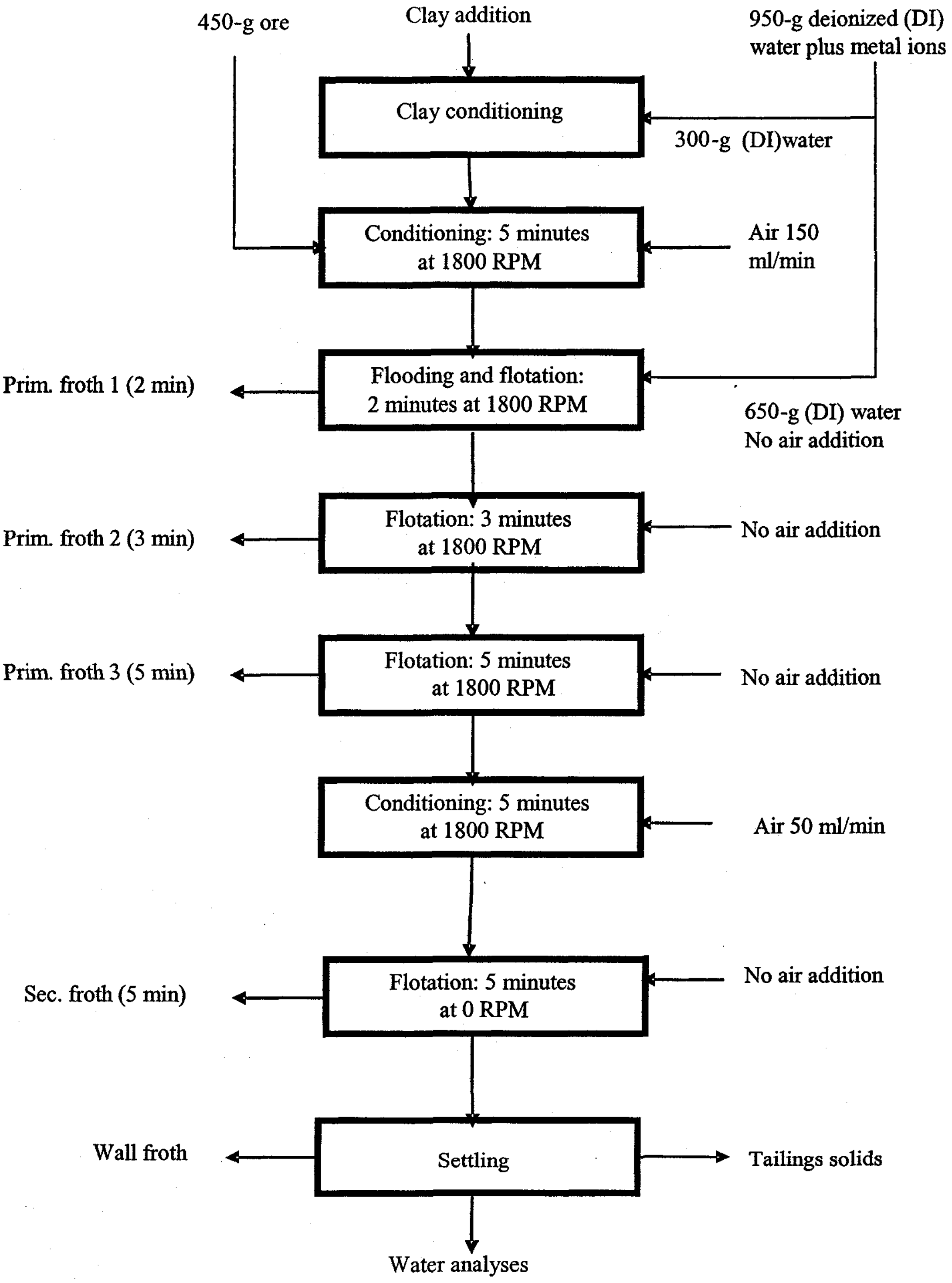


Figure 3-3: Diagram of the doping tests and procedure

3.2 Doping Tests

3.2.1 Primary Conditioning

Solutions of divalent metal ions (Ca^{2+} or Mg^{2+}), from the corresponding chloride salts, were prepared at desired levels of concentration for doping tests by dissolving chemicals into 2 liters of deionized water or any other water source tested as the flotation process water or the tap water (Kasongo et al., 2000). To ensure proper preparation of additives and reproducibility of concentrations within ppm ranges, solutions were prepared using calculated dosages and dilutions shown in Table A2-1 in page 196 for calcium from $CaCl_2.6H_2O$ and Table A3-1 in page 197 for magnesium from $MgCl_2.6H_2O$. Solutions were prepared right before test runs to minimize any transient solution change. Three types of clays (kaolinite, illite, and montmorillonite) were tested at 1 wt% with respect to the weight of the ore sample (Kasongo et al., 2000).

The total amount of clay powder, for doping tests at the desired percentage of ore, was added to the warm water and was dispersed completely under mechanical agitation. Montmorillonite clay tends to form clogs that stick to surfaces and do not disperse in the slurry. The suspension of clays in solutions that contained calcium ions were stabilized at the desired temperature of 76°C in the cell. The temperature was controlled by the circulation of hot water from the heating bath through the water jacket. To ensure uniformity in the properties of the feed ore for each experiment, the frozen sample was allowed to thaw at room temperature for 30 minutes immediately before the test. To the 300 mL warm suspension, 450 g of thawed ore sample was added, bringing the slurry density to around 60 % oil sand by weight. The remaining ore sample was kept as head sample for analysis. The slurry was mechanically agitated at 1800 rpm, during which air was injected and dispersed through the slurry by the rotor. The air flowrate was set at 150 mL/min. The bottom valve of the visualization glass tube was opened to allow the bubbles to rise through clear water in the glass tube and to be recorded. Conditioning of the slurry continued for an additional 5 minutes, after which the air injection was stopped while mechanical agitation continued at 1800 rpm.

3.2.2 Primary Flotation

To lower the slurry density to 32 % oil sand by weight, 650 mL of prepared solution was added to the cell while continuously agitating the slurry at 1800 rpm. As outlined in Figure 3-3, bitumen froths were removed as a function of time and collected into froths of 2 minutes, 3 minutes and 5 minutes periods for a total of 10 minutes primary flotation for the kinetics study (Somasundaran, 1975). At the end of a total 10 minutes primary flotation period, agitation was stopped to skim off all the primary froth that was added to the third froth product (prim. froths).

3.2.3 Secondary Flotation

Mechanical agitation was restarted at 1,800 rpm for 5 minutes with air injection at 50 mL/min. The air injection and mechanical agitation were then stopped for removal of the accumulated secondary froth. During the whole test period, the pulp level was not controlled and no makeup water was added.

3.2.4 Wall Froth

The remaining tailings slurry was removed from the cell. All the bitumen sticking on cell walls and shaft surfaces was washed off using toluene and reported as wall froth.

3.2.5 Sample Treatment

The head sample and all five froth samples collected were weighed. The bitumen, solid and water contents were determined for each of the samples. For the wall froth sample, only bitumen content was determined. The results of the analyses were used for calculating bitumen recoveries and evaluating froth quality. The feed water and process water were also analyzed and used for surface tension, contact angle and induction time measurements. Prior to analysis, the process water was centrifuged to remove suspended solids.

3.2.5.1 Determination of Bitumen, Solid and Water Contents

The Dean Starke method was used to determine the bitumen, solid and water contents. For most of the tests, only bitumen contents were determined using the procedures described by Dai and Chung (1996). In this method, bitumen was dissolved in a known volume of toluene at bitumen to toluene mass ratio between 0.12 and 0.25. A desired amount of water was added to facilitate phase separation. The mixture, in a sealed bottle, was shaken using a mechanical shaker (Fisher) for 30 minutes. The mixture was then left still overnight to ensure complete dissolution of bitumen in the toluene and to allow for complete phase separation. About 30 mL of the organic phase was centrifuged at 35,000 g-force for 30 minutes to remove the entrained water and solids. About 15 mL of the diluted bitumen at the upper portion of the centrifuge tube was weighed accurately and transferred to a glass vessel. The toluene in the sample was allowed to evaporate in a vacuum oven at 50°C for 48 hours. The weight of the residue after such toluene evaporation was considered to be the amount of bitumen dissolved in the sample. The bitumen content in froth was then calculated from the known volume of toluene added times the ratio of bitumen to toluene determined as such.

3.2.5.2 Bitumen Recovery

Bitumen recovery (R) is the percentage of the total bitumen contained in the feed sample that is recovered to the froth (Wills, 1997). Mathematically, it is given by:

$$R = \left(\frac{bitumen\ weight\ in\ the\ froth}{bitumen\ weight\ in\ the\ flotation\ feed}\right)x100\% \tag{3-1}$$

A high R-value indicates a good bitumen recovery, meaning that a high proportion of bitumen in the feed reports to the froth.

Let F, F_2, F_3, F_5, F_S, F_W, and T be the masses of the feed sample, 2-minute froth, 3-minute froth, 5-minute froth, secondary froth, wall froth and tails, with their respective bitumen contents being f, f_2, f_3, f_5, f_S, f_w, and t.

Mass balance leads to:

$$F = F_2 + F_3 + F_5 + F_S + F_W + T, \tag{3-2}$$

while the bitumen balance is:

$$F\,f = (F_2\, f_2) + (F_3\, f_3) + (F_5\, f_5) + (F_S\, f_S) + (F_W\, f_w) + (T\, t). \tag{3-3}$$

Incremental recoveries are expressed as:

$$R_t = \frac{F_t f_t}{Ff} x100\% \tag{3-4}$$

with t = 2, 3, 5, S (secondary), W (wall froth).

The primary recovery is defined as:

$$R_p = \frac{(F_2 f_2) + (F_3 f_3) + (F_5 f_5)}{Ff} x100\% \tag{3-5}$$

while the secondary recovery is defined as:

$$R_s = \frac{F_s f_s}{Ff} x100\% \tag{3-6}$$

The combined primary and secondary recovery is:

$$R_p + R_s = \frac{(F_2 f_2) + (F_3 f_3) + (F_5 f_5) + (F_S f_S)}{Ff} x100\% \tag{3-7}$$

The total recovery includes the wall froth recovered, i.e.

$$R_{total} = \frac{(F_2 f_2) + (F_3 f_3) + (F_5 f_5) + (F_S f_S) + (F_W f_W)}{Ff} x100\% \qquad (3\text{-}8)$$

The incremental recovery data allows us to examine bitumen flotation kinetics by fitting the data to models analogous to chemical reaction kinetics, often described by a first-order rate process (Lynch, 1981). Hot water and low energy extraction processes target the best operating conditions that allow maximum bitumen recoveries (R_M) achievable over entire flotation time that is available for processing. The objectives are to achieve optimum selectivity in separating bitumen from sands, and to produce high froth quality by maximizing bitumen content while minimizing solid and water contents. Since bitumen is highly hydrophobic, bitumen would exhibit fast flotation kinetics under ideal operating conditions (Xu, 2003). For batch flotation tests, cumulative recovery varies with flotation time (t) in a first order rate equation (Zhou, 2003; Finch, 1990; Wills, 1997; and Zhou, 2004) as:

$$R_t = R_M . (1 - e^{-\kappa t}) \qquad (3\text{-}9)$$

where R_t (%) is the cumulative recovery after a flotation time t, R_M (%) is the maximum flotation recovery achievable and κ (time^{-1}) is the flotation rate constant under a given flotation condition. These parameters can be estimated by fitting the experimental results to the first order rate equation shown above.

Throughout this study, we have preferentially considered the primary recoveries as being more sensitive to the effects of changes of variables than the total recovery that could mask possible effects of certain variables (Horsley, 1951).

3.2.5.3 Froth Quality

The froth quality, (Q), or bitumen grade of flotation froth, is used to evaluate the selectivity of the bitumen flotation process. It is defined as:

$$Q = \left(\frac{\text{the mass of bitumen in the froth}}{\text{the mass of the froth}}\right) x100\% \tag{3-10}$$

A high Q value corresponds to a good froth quality containing less solid and water.

The primary froth grade (f_p) equals:

$$f_p = \frac{(F_2 f_2) + (F_3 f_3) + (F_5 f_5)}{F_2 + F_3 + F_5} x100\% \tag{3-11}$$

The grade of the combined primary and secondary froth (f_{ps}) is:

$$f_{ps} = \frac{(F_2 f_2) + (F_3 f_3) + (F_5 f_5) + (F_S f_S)}{F_2 + F_3 + F_5 + F_S} x100\% \tag{3-12}$$

The grade of the total froth (f_{total}) including the wall froth recovered is:

$$f_{total} = \frac{(F_2 f_2)+(F_3 f_3)+(F_5 f_5)+(F_S f_S)+(F_w f_w)}{F_2+F_3+F_5+F_S+F_w} x100\% \qquad (3\text{-}13)$$

3.2.5.4 Contact Angle Measurements

To assess the change of hydrophobicity of a bitumen surface due to slime coating during flotation with and without additives, the static and dynamic contact angle were measured using a captive bubble method (Fujimoto 1985; Zhou et al., 1998). In each case, a layer of coker feed bitumen or fresh bitumen froth obtained right after bitumen flotation was spin coated on a methylated glass slide or Teflon surface. The smooth bitumen-coated surfaces were then immersed in suspensions made of de-ionized water or process water containing 0 to 0.5% clays with or without calcium ion addition. The variations could simulate bitumen-clay interactions in the extraction process under various conditions. The suspensions were heated at 76°C and vigorously stirred in a beaker with a magnetic stirrer for 20 minutes. The bitumen layer on the glass or Teflon slide was transferred into a square glass vessel (3 x 3 cm) containing the proposed suspensions. The cell was equipped with a water jacket to control temperature. An air bubble was subsequently generated at the tip of a micro-syringe shown in Figure 3-4 and pushed down to contact the surface of the bitumen.

In this study, the water receding contact angles of an air bubble on bitumen in water were considered to be most representative of bitumen-bubble attachment in a flotation process. They were measured with an optical microscope in a Rame Hart goniometer through the water phase from both sides of the air bubble attaching to bitumen. The measurements of

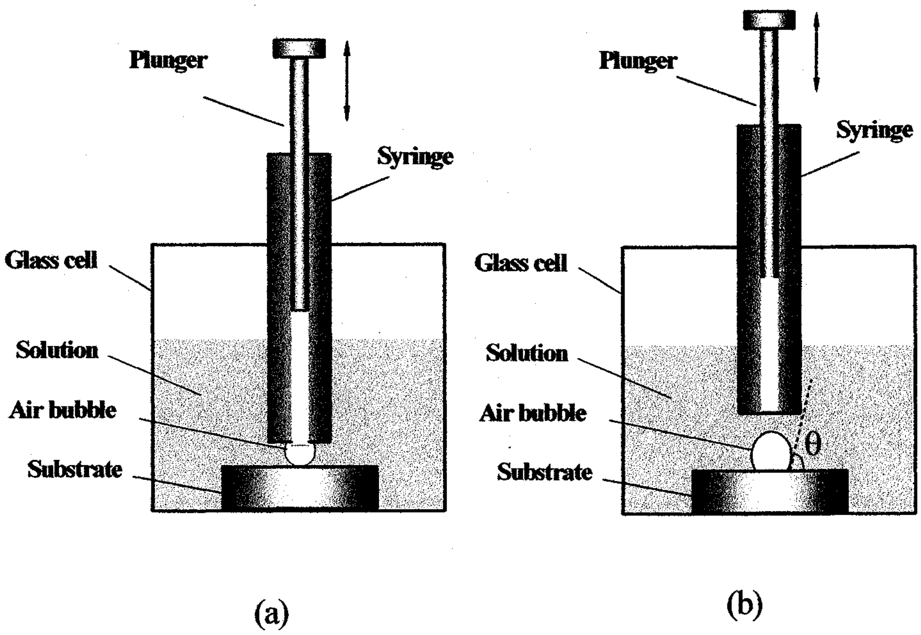


Figure 3-4: Schematics of contact angle measurement after Liu (2003)

the static contact angle were repeated and averaged. To assess the strength of bitumen-air bubble attachment, photographs were taken for a bubble approaching and retracting from a bitumen surface.

At room temperature, the contact angle was relatively easy to measure using the procedures described above. At high temperatures, measuring contact angle is much more challenging due to spontaneous spreading and engulfing of bitumen on the air bubble. In this case, estimation of the tangent to the air bubble surface at the contact point becomes a source of error. Under these conditions, the attachment process was recorded and the contact angle was measured from recordings played on the TV screen by means of a transparent protractor and scale. The values from both sides of the bubbles were averaged.

3.2.5.5 Surface Tension of Supernatants

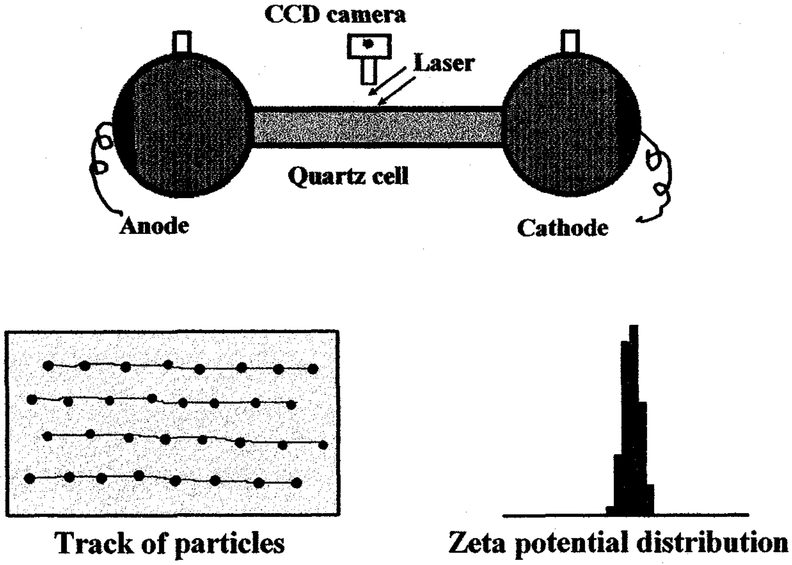
The objective of measuring the surface tension of the process water was to determine whether there is any correlation between the surface tension of the flotation pulp supernatant and bitumen recovery.

The value of surface tension serves as an indicator for natural surfactant release. Therefore, measuring the surface tension of the flotation pulp supernatant would allow us to elucidate the role of natural surfactant release in bitumen flotation (Shaw, 1999; Osipow, 1962). The supernatant is the process water remaining after flotation. During doping tests, no other water was added to the flotation cell. The tails slurry after secondary flotation was transferred from the Denver flotation cell into a 1-liter jar for settling of the solids. Water was decanted and centrifuged in Nalgene Teflon bottles at 35,000 g-force to separate the suspended fines. The clear supernatant was then stored in a clean jar for surface tension and induction time measurements.

Two techniques are commonly used to measure surface tension: the Wilhelmy Plate Method and the de Noüy Ring Method (de Noüy, 1909). Both techniques are based on measuring the forces required to make the ring or the plate traverse the interface between water and air. In this study, the surface tension was measured by an automated process tensiometer (Krüss K12). The measurement was performed at room temperature, although the bitumen extraction tests were performed at higher temperatures.

3.2.5.6 Measurements of the Zeta Potential of Suspended Particles

Zeta potential is one of the most important surface properties in a colloidal system. The objective of measuring the zeta potential is to study the role of the electrostatic forces affected by water chemistry in bitumen recovery and to explain the association of solids with bitumen in froths. The phenomenon of slime coating was discussed by Finkelstein et al., (1975); Fuerstenau, (1985 p. 150); Takamura and Wallace, (1988); and Schramm et al., (1985). It is referred to as the build up of hydrophilic barriers that prevent direct contact of air bubbles with hydrophobic bitumen surfaces; they cause a reduction of bitumen recovery (Jameson, 1984; Raghavan, 1975; Sutherland and Wark, 1955; Warren, 1975; Jameson, 1984). In our study, the zeta potential was measured with a Zetaphoremeter III (SEPHY/CAD) as shown in Figure 3-5. The measurement was



Track of particles

Zeta potential distribution

Figure 3-5: Schematic of zeta potential measurement after Liu (2003) described by Liu (2003) as a technique to study the colloidal interactions between oil sand components and slime coating of fines on bitumen surfaces. The Zetaphotemeter consists of a rectangular electrophoresis cell; a pair of hydrogenated palladium electrodes, a laser-illuminator, an optical microscope and a digital video image capture viewing system (CCD camera). The computerized operating system allows for accurate positioning of the optical microscope view field at the stationary layer for accurate measurement of electrophoretic mobility.

In this study, about 40 ml of the prepared particle suspension or oil/bitumen emulsion was used to fill the electrophoresis quartz cell. Great care was taken to avoid trapping air bubbles. Through the laser-illumination and video-viewing system, the movement of the droplets or particles under the applied electric field in the stationary layer was traced, 5 times for each direction by alternating positive/negative electrode potentials. The captured images, as shown schematically in Figure 3-5 by the track of the particles, were then analyzed by the built-in image processing software.

A unique feature of this instrument was that it can trace 50-100 particles simultaneously each time, and a distribution histogram of electrophoretic mobility or zeta potential for these particles was provided. Zeta potential (ζ) was calculated from the measured electrophoretic mobility by the Smoluchowski equation (Van Olphen, 1963) shown in section 2.4.6 by the equation (2-13). The measurement error was generally less than 5 %, except for high electrolyte concentrations above 10^{-2} M, in which case the error was as high as 10 %. In the case of a binary mixture, the measured average zeta potentials of the two components often over or under estimate the electrokinetic behavior of the system. Interpretations of zeta potential distribution measurement results (Liu et al) help identify the deposition condition of one component on the other in a binary suspension. More importantly, this surface property-based technique does not suffer from the limitations of particle density and geometry.

3.3 Visualization of Bitumen Loading on Air Bubbles

3.3.1 Literature Review

In mineral flotation, efforts have been made to develop techniques for on-line characterization of bubbles. Several authors studied entrainment of minerals in mechanical flotation cells. The imaging methods used included optical devices, electronic sensors and photographic techniques. Most of the imaging techniques and computer-controlled microscopic techniques capture images from the froth surface to analyze its appearance, color, surface reflectance, air bubble size and texture (Barrera-Godinez, 1990; Guarini, 1994; Moolman, 1996). The information derived is used as indicators to detect potential problems in flotation, and to evaluate metallurgical performance such as flotation recovery and concentrate grade. Bonifazi (2002) used a three-dimensional (3D) froth surface image characterization technique to determine flotation recovery and concentrate grade. Based on an image analysis method, the Julius Kruttschnitt Mineral Research Centre (JKMRC) in Australia developed the JKFrothCam technology (Holtham, 2002) for the mineral industry. Dynamic image analysis methods were also developed to measure materials carried into the overflowing froth (Ventura-Medina, 2002).

To date, considerable efforts have been made to visualize the attachment of minerals to air bubbles in base metals processing (Cynthia et al. 2001). However, the existing methods applied to mineral systems are not suitable for bitumen extraction systems. This is because the froth layer in bitumen extraction system is dark, opaque, and subtle differences in froth appearance are not apparent. In the oil sands industry, emphasis is made on the characterization of aggregates inside the separation vessel in terms of number of aggregates floating and reporting to the froth layer, and the size, shape and rising velocity of bubble–particle aggregates (Malysa, 1999). The impinging jet technique provides a direct observation of the attachment process of micro bubbles onto a solid surface in real time under varying physicochemical conditions (Yang, 2000). This method was first applied to a model system using methylated glass to simulate a bitumen surface that is bombarded by a jet of air bubbles; the subsequent attachment was observed. In oil sands laboratory and commercial plants, such a device to visualize the strength of attachment between air bubbles and bitumen in water is not available.

Our study closes this gap by working with a real system and developing a novel on-line visualization technique based on the concept of the Syncrude Luba tube. The concept was previously developed at Sycrude Canada Ltd. (Zhou, 2000) for plant performance diagnosis using images collected from inside the froth layer. Our visualization technique uses images taken from the bulk slurry during the early stage of conditioning. It allows the changes in the strength of attachment between air-bubbles and bitumen droplets to be visualized and used as an indicator of changes in the metallurgical performance of separating bitumen from sands.

3.3.2 Description of the Visualization Tube

The visualization unit shown in Figure 3-6 is a rectangular Pyrex glass tube: 24 mm wide, 8 mm thick and 80 mm high with a ruler attached on the back surface for size measurements. The bottom of the rectangular glass tube is fused onto an 8-mm diameter and 100 mm long glass tube. The glass tube is inserted into the flotation cell vertically with the sampling port being positioned 25 mm above the bottom of the cell and 25 mm from the sidewalls of the cell to avoid the "wall effects" (Happel and Brenner, 1973). The tube is installed in vertical position with a given distance away from the walls in order not to disturb the motion and the velocity of aggregates when they rise inside the confined space of the tube. The tube was filled with clear water with a specially designed Teflon plug at the bottom to block the inlet from premature penetration of slurry. Pulling up or pushing down on the Teflon plug allowed the inlet of the tube to be closed or opened at a desired time during the experiments. The gap between the inlet of the tube and the plug at open position was maintained at about 15 mm to obtain a representative sample of bubble-particle aggregates within the flotation cell. The upper end of the rectangular tube was fused on to an 8-mm inner diameter and 120 mm long L-shape glass tube. The free end of the tube was connected to a reservoir with a column of water that was under vacuum to maintain water inside the observation cell above the slurry level. This design allowed air bubble-bitumen aggregates to rise freely, be visualized inside the clear water, and be captured above the slurries in the opaque steel cell.

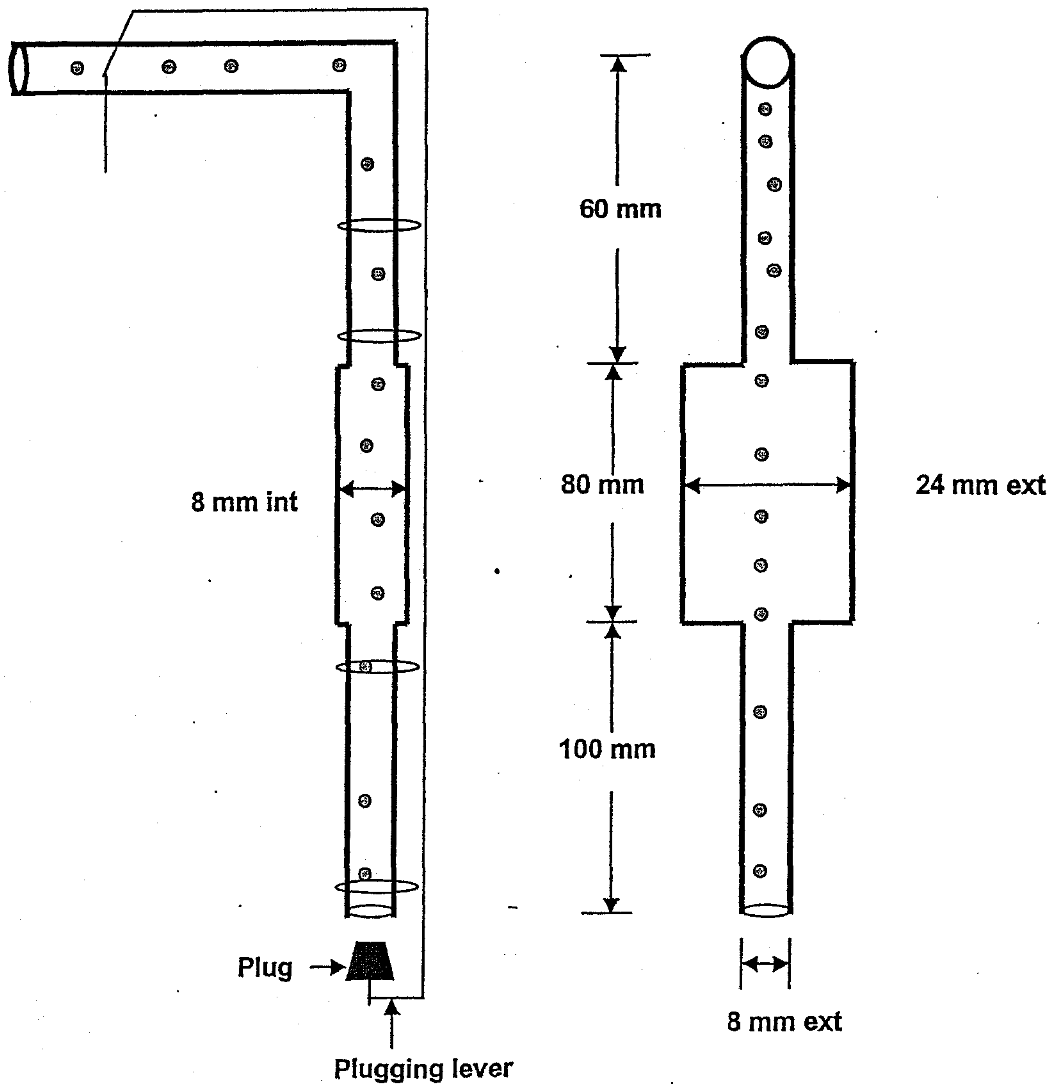


Figure 3-6: Visualization glass tube

3.3.3 Experimental Procedure

Prior to each test, the clear water at a desired temperature was sucked from the cell into the glass tube and held in place under the suction force of a low level vacuum that was achieved in the laboratory set up shown in Figures 3-1 and 3-2. The plug was positioned to close the inlet. At the beginning, slurries were gently mixed by hand with a spatula before injection of air to minimize the entrapment of air from the atmosphere. Early during conditioning of the slurries with air injection, the holding plug at the bottom of the tube was pushed down to open the sampling port of the tube.

To ensure clear visibility of the aggregates in the observation area, recording was started immediately. A longer delay would allow slimes to reach the recording zone and make the images unclear. Bubbles and aggregates of aerated bitumen that entered the tube rose vertically to the level of the observation area, 2 cm x 2 cm in width and 8 mm in depth. A high resolution and high frame-rate CCD color camera PULNIX was used to capture images. The recording system was equipped with a macro-zoom lens, placed perpendicular to the rising flow of the aggregates. A 500 W halogen lamp placed beside the camera provided the necessary lighting. Images were viewed on line using a Sony Trinitron color TV monitor and recorded with a shutter-speed greater than 1/1000s using a VHS-SVT-S3100 time lapse 168 SONY VCR that featured 60 fields per second. This was the minimum speed required to record large size bubbles for the determination of bubble rising velocity on the frame-by-frame playback mode.

3.3.4 Image Analysis

The size and rising velocity of air bubbles and air bubble-bitumen aggregates were determined by transferring the recordings from the video tape to an electronic format using commercial Snappy Video Snapshot applications that grabbed and digitized recorded images. The digitization of recorded images allowed for quantitative analysis using the Sigma Scan Pro automated image analysis software, to determine the shape, size and rising velocity of aggregates. The Feret bubble diameter, calculated for each aggregate, was defined as:

$$d_F = \left(\frac{4.Area}{\pi}\right)^{\frac{1}{2}} \tag{3-14}$$

The d_F determined as such represents an equivalent diameter of a fictitious spherical object that would have the same volume as the irregular object being considered.

3.3.5 Application to Coal Flotation.

The visualization technique is a powerful tool to help studying flotation processes. It was used to visualize the separation of coal particles from its gangue in deionized water as shown on the screen in Figure 3-2 to help understanding the separation of bitumen from sand. Coal and bitumen are characterized by similar natural hydrophobicity and inherent floatability that characterize also only talc, graphite, molybdenite, and sulfur. Coal floats with strong attachment to the air bubbles to separate from its gangue of kaolinite, illite, montmorillonite clays and silicates (Aplan, 1966; Weiss, 1985). These clay minerals are responsible for the slime coating effect that decreases the attachment of coal to air bubbles, reducing its hydrophobicity and causing depression of yield and recoveries. The refractoriness toward floatation increases for oxidized coal and 1% caustic soda addition restores depressed yield as observed for bitumen recoveries in the doping tests under similar pHs in the range 7-8.

Our visualization technique and the study by Ata and Jameson (2005) have contributed to the understanding of mechanisms that impact the yield and grade of produced coal during flotation. Their study helped to suggest that during coal flotation, the formation, the stabilization and the strength of the air bubble clusters to resist to the breakage during rise to the froth zone depends on the dosage of dodecylamine (DDA) the collector used for silica, the dosage of methyl isobutyl carbinol (MIBC) the frother, and the grades of coal and of silica. This study suggests that the rate of growth of aggregates air bubbles-coal increases with the increase of the diameter of air bubbles and with the change of their shape. This suggests that flotation is completed by the capture of individual coal particles by individual air bubbles and then each particle is attached to multiple bubbles. This suggests that the growth of aggregates air bubbles-coal is due to the attachment of more particles by air bubble. This would correspond to high yield but poor selectivity because of entrainment of non floating particles to the froth zone. In our study, we have observed formation of cluster with entrainment of silica particles in the size range (-210, +150) μm as result of collector addition.

3.3.6 Conclusions on the Visualization Technique

This visual observation technique applied to coal flotation provides, in real time, a qualitative overview of its selective concentration and transfer to the froth zone. This imaging technique allows describing the phenomenological understanding of strength of attachment of coal to the air bubbles to form rising aggregates and understand mechanism of non-selective entrainment of non floatable species to the froth layer. In this work, we will expend this knowledge from coal to bitumen flotation from oil sands.

CHAPTER 4

RESULTS AND DISCUSSION

In this study, we were not concerned about the optimal flotation conditions, but about the role of various additives and operating conditions on bitumen recovery. The objective was to identify key variables and their limit for determining oil sands ore processability. Variables we have considered in this study are: changes of water chemistry in terms of the concentrations of ions (Ca, Mg, Na, $NaHCO_3$), changes of ore characteristics, kaolinite, illite, montmorillonite contents in the ores; and interactions between metal ions and clays. Other operating variables considered are ore grades, operating temperatures, process aids (caustic, bicarbonate, LEE chemicals), mechanical energy, air addition, circulating loads of fines, and the occurrence of refractory ores known as poor processing ores, transition ore, oxidized ore, and low grade ores.

4.1 Major Findings from this Research Work

Preliminary factorial design experiments were performed as screening tests to identify the effects of two factors, montmorillonite clay content in ores and calcium ions in water, and their interactions on bitumen recovery. Each factor had 2 levels: 0 and 1wt% montmorillonite clay additions to the feed ore samples and 0 and 40 ppm calcium ion concentrations in water. Series of one-factor-at-a-time and crossed factorial experiments were conducted. With such a small number of factors, graphical analysis is preferred to statistical methods of variance analyses (Montgomery, 1996). Table 4-1 and Figure 4-1 summarize replicates of primary recovery produced in response to changes in the levels of montmorillonite clay additions to the ore samples and calcium concentrations in water. At the baseline conditions of 0 ppm Ca and 0% montmorillonite clay addition, 95.2% bitumen recoveries are achieved. At the low level of 0 ppm calcium, an increase in montmorillonite clay contents to 1% of ore decreases bitumen recovery only marginally from 95.2% to 91.4%. At the low level of 0% montmorillonite clay content, an increase of calcium ion concentration from 0 to 40 ppm in process water decreases bitumen recovery marginally from 95.2% to 92.5%. This finding indicates that there is only a marginal effect by changes in individual parameters on bitumen recovery.

Table 4-1: Effects of changes in additives (calcium ions and montmorillonite clay) on bitumen recovery

Bitumen Rec. (%)	0% Mont. Clay	1% Mont. Clay	Average
0 ppm Calcium	95.2	91.4	93.3
40 ppm Calcium	92.5	59.3	75.9
Average	93.9	75.4	

However, at 40 ppm calcium addition, doping 1 wt% montmorillonite clay into the ore caused a significant decrease in bitumen recovery from 92.5% to 59.3%. Alternatively, at the high level of 1% montmorillonite clay the response in bitumen recovery to the increase of calcium ions from 0 ppm to 40 ppm ions in water shows also significant

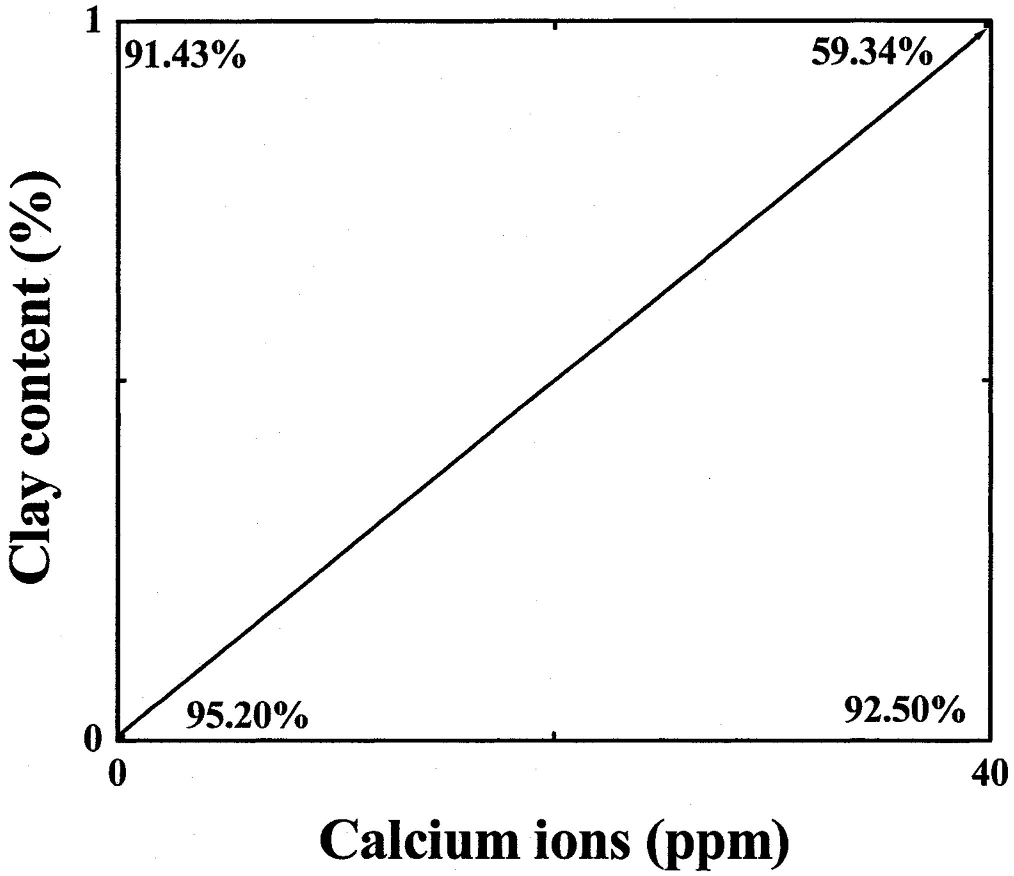


Figure 4-1: Factorial design results of the effects of additives doped individually and added together on bitumen recovery using deionized water at 76°C

decrease of 32.1% bitumen recovery from 91.4% to 59.3%, in comparison to a marginal decrease of 2.70% in bitumen recovery at 0 % montmorillonite clay. These variations are illustrated graphically by two non-parallel curves drawn in Figure 4-2, showing bitumen recovery against two levels of calcium concentration and montmorillonite clay addition. The non-parallel nature of the lines is an indication of interactions between the two factors, calcium ions and montmorillonite clay that affect bitumen recovery (Montgomery, 1996). When the two variables change, the value of Montgomery's main effect concept for calcium ions is the difference between the average bitumen recoveries at the low level of calcium (93.32%) and the average bitumen recoveries at the high level of calcium (75.92%). It shows a decrease of bitumen recovery by 17.39 %. A similar decrease of bitumen recovery is observed as the main effect of fine montmorillonite clays. However this effect was not observed with kaolinite and illite clays and it is worth mentioning that one of our major contributions is demonstrating the importance of type of clays that specifically affect bitumen recovery.

4.2. Bitumen Recovery in Baseline Conditions of Hot Water Extraction Processes

Under baseline conditions at 76°C for good processing ore samples averaging 10.57 % bitumen from Syncrude Mildred North Mine, bitumen recovery was repeatedly reproduced with an excellent low range error at 1.5 % shown by the error bars on the Figure 4-3. The solid curve of obtained bitumen recovery (R_t) shows its best fit to the first order rate equation:

$$R_t = R_{\infty}\left[1 - e^{-K(t+\tau)}\right] \tag{4-1}$$

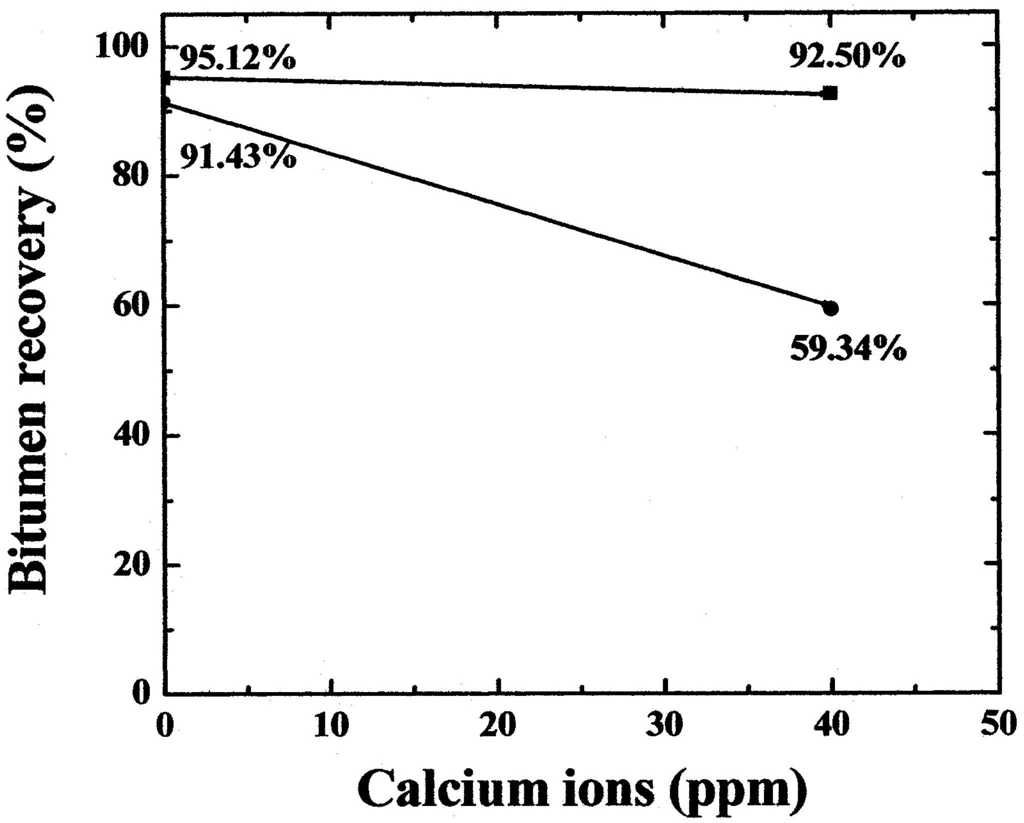


Figure 4-2: Effect of Ca^{2+} concentrations in deionized water at 76°C in the absence and in the presence of 1% montmorillonite clay doped to good processing ore on bitumen recovery

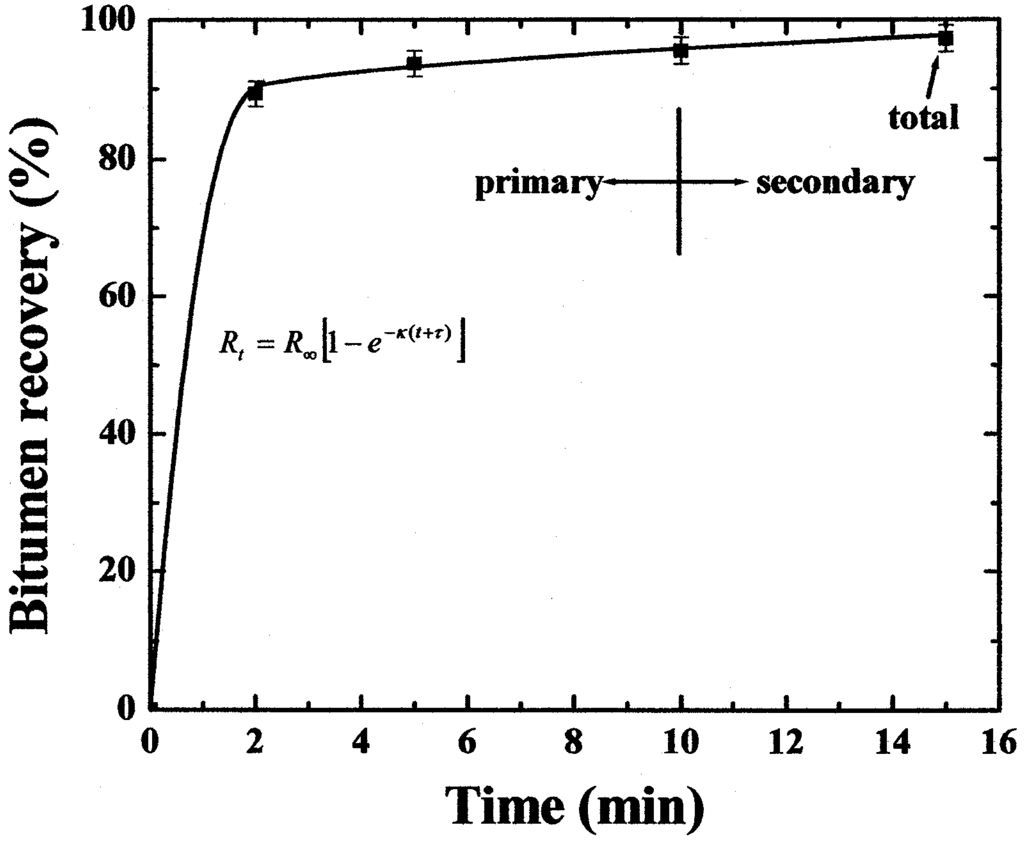


Figure 4-3: Repeatability of bitumen recovery using the laboratory Denver cell for good processing ore sample under baseline flotation conditions with deionized water at 76°C without additives

Where t is the flotation time (min), τ the zero time correction factor (min), R is the recovery at time t (min), R_∞ the recovery at time infinite (%) and κ is the flotation rate constant (min^{-1}).

The figure shows fast process kinetics with about 90% of bitumen being recovered within 2 minutes of flotation (Agar et al., 1980; Xu et al., 1996), resulting in a rate constant κ of 1.1 min^{-1} (Kasongo, 2000). The curve shows that the total flotation time is sufficient for an appreciable quantity of bitumen to be recovered.

4.3. Effect of Metal Ions on Bitumen Recoveries without Clay Addition

4.3.1 Effect of Monovalent Cations (Na^+) on Bitumen Recoveries

In laboratory tests, 40, 400, 800, and 1000 ppm Na addition from NaCl had a marginal effect on bitumen recovery as shown by our results in Figure 4-4 for high grade ores compared with previous studies on medium and on low grade ores. This finding suggests that below 1000 ppm, the effect of monovalent sodium ions alone is marginal. Studies on medium and low grade ores suggests that by increasing the concentration of monovalent sodium cations, bitumen recovery will be depressed. Thus the ionic strength of the slurry alone cannot be used to explain and predict the effect of water chemistry on bitumen recovery. In the commercial operations, monovalent ions such as sodium (Na^+) and potassium (K^+) are released from minerals and their concentration builds up in recycle pond water that is reused in bitumen extraction (Syncrude, 1998). Sodium is also introduced by caustic used as process aid.

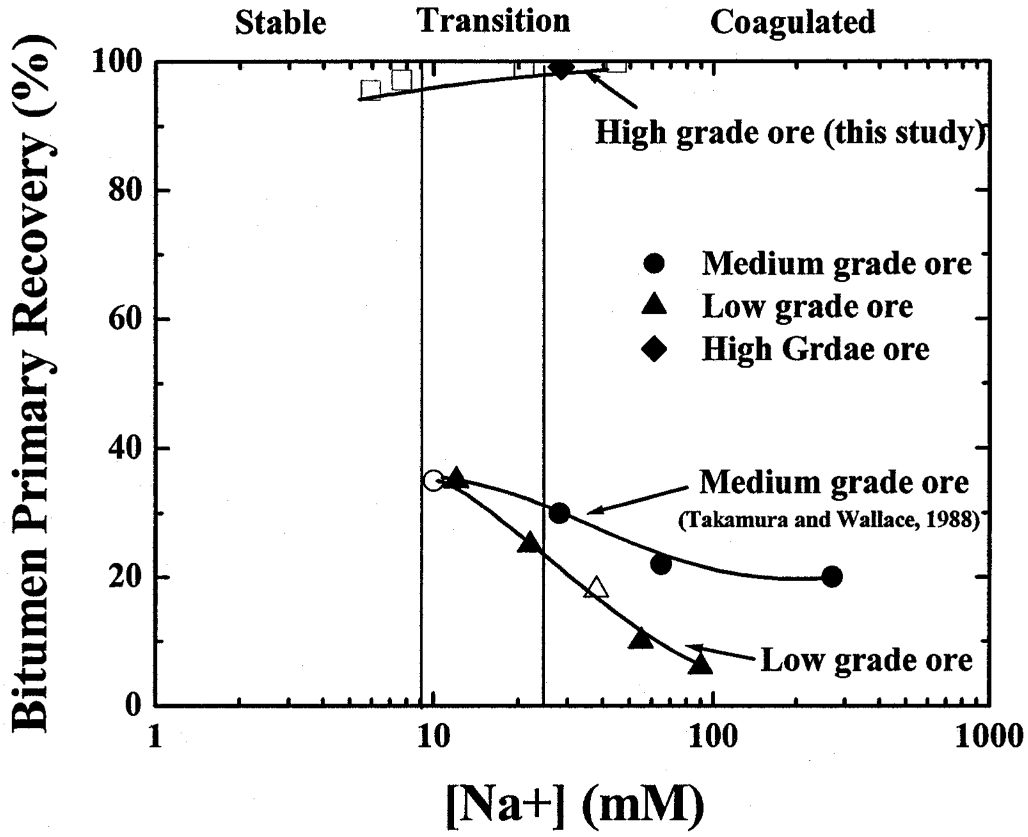


Figure 4-4: Effect of sodium Na^+ ion concentrations doped alone in deionized water at 76°C to high grade ore compared to previous tests with medium and low grade ores on bitumen recovery

4.3.2 Effect of Divalent Cations (Ca^{2+}) on Bitumen Recoveries

Figure 4-5 shows that bitumen recovery decreases marginally from the baseline conditions when calcium ions are dissolved in feed water at 40 ppm. This marginal change in bitumen recovery is within the range of experimental error of typical flotation tests. This finding is in agreement with plant observations of experiencing marginal changes of bitumen recovery due to variation of calcium ion contents in feed water (0-40 ppm) when low fine ores are processed (Cox, 2000).

4.3.3 Effect of Clays Addition Alone on Bitumen Recoveries

Figure 4-5 shows also the effect of montmorillonite clay addition alone on bitumen recovery at 76°C. As seen with the addition of calcium ions alone, bitumen recovery decreased only marginally when montmorillonite clay addition was increased from 0% to 1% of the oil sand ore by weight. Similar observations were made with kaolinite and illite clays additions. These results suggest that the recovery will divert only marginally from the baseline recovery for good processing ores when metal ions are added or when clays are doped individually at 1% of the oil sand ore by weight. This is an important finding as commercial oil sands operators use bitumen grades and fines contents as markers to define processability (Sanford, 1983). The clay contents of fresh good processing oil sand ores is generally low, but it will increase in the PSC (primary separation cell) feed stream as a result of a high total suspended solids content in recycle water used for dilution, and as a result of the circulating load of fines from primary and secondary flotation froths in LEE processes (Albian Process).

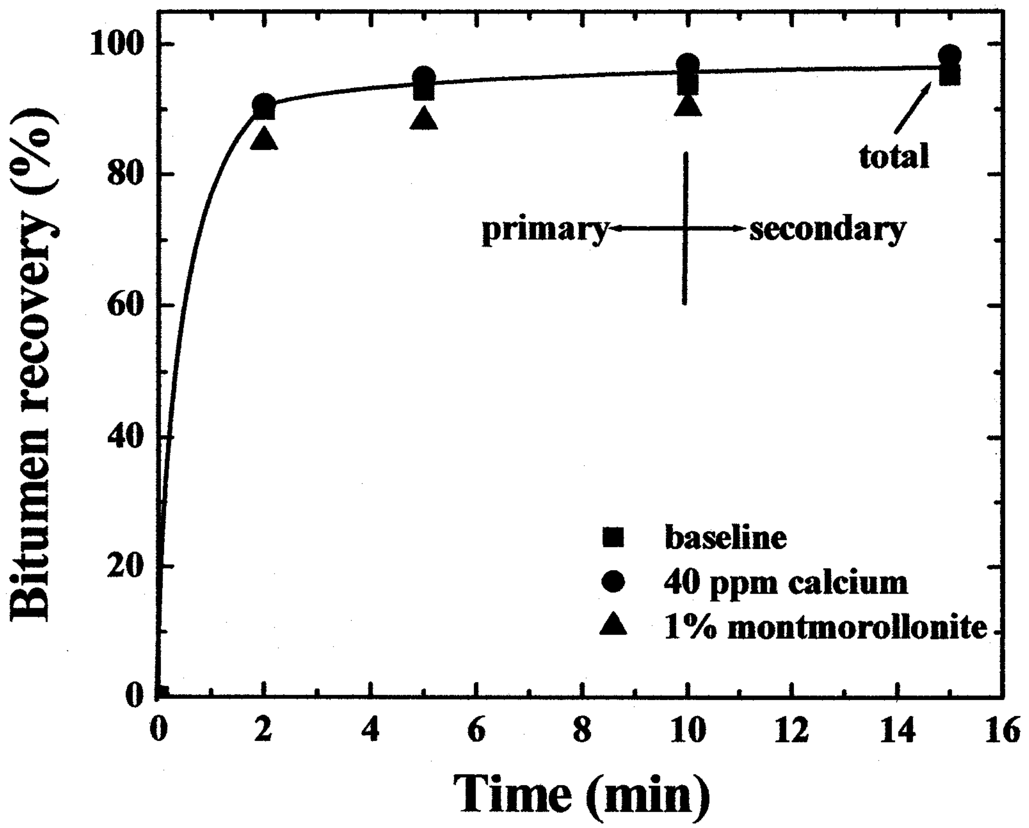


Figure 4-5: Effect of Ca^{2+} ions and of 1% montmorillonite clay doped individually to good processing ore in deionized water at 76°C compared to bitumen recovery under baseline conditions

4.3.4 Effect of Clays-Metal Ion Co-addition on Bitumen Recoveries

After doping a good processing ore with 1 % montmorillonite clay in the presence of calcium ions dissolved in the feed deionized water from $CaCl_2$, Figure 4-6 showed a significant depression of bitumen recovery when calcium ion concentration was increased higher than 30 ppm. At 40 ppm Ca^{++} addition, bitumen recovery was depressed by 26% to about 70%. This recovery shown for good processing ore doped with calcium at 40 ppm in Figure 4-6 corresponds to the one encountered for poor processing ores such as low grade ores shown and that is characterized by (11-16) ppm calcium content. Bitumen recovery is affected by the interaction between metal ions in water and fine clays from the ore doped. As suggested for coal processing (Arnold and Aplan, 1986; Xu, 2003; Brown and Smith, 1954, Burdon, 1976; Mishra, 1978) this reduction in bitumen recovery suggests the occurrence of slime coating of a layer of hydrophilic clay particles on hydrophobic bitumen surfaces, preventing the attachment of bitumen with air bubbles.

4.3.5 Effect of Changes in Calcium Solubility on the Interaction Clays-Metal Ion and Bitumen Recoveries

Decreasing the solubility of calcium ions in water will decrease the depression of bitumen. We have studied the effect by comparing higher solubility compounds used during this study as hydrous $CaCl_2.6H_2O$ and anhydrous $CaCl_2$, with lower solubility compounds as calcite $CaCO_3$ and gypsum $CaSO_4$. Figure 4-7 shows important effect when anhydrous $CaCl_2$ is used to dissolve calcium and a marginal impact on recovery when good ore is doped with calcium from less soluble compounds as calcite $CaCO_3$ and

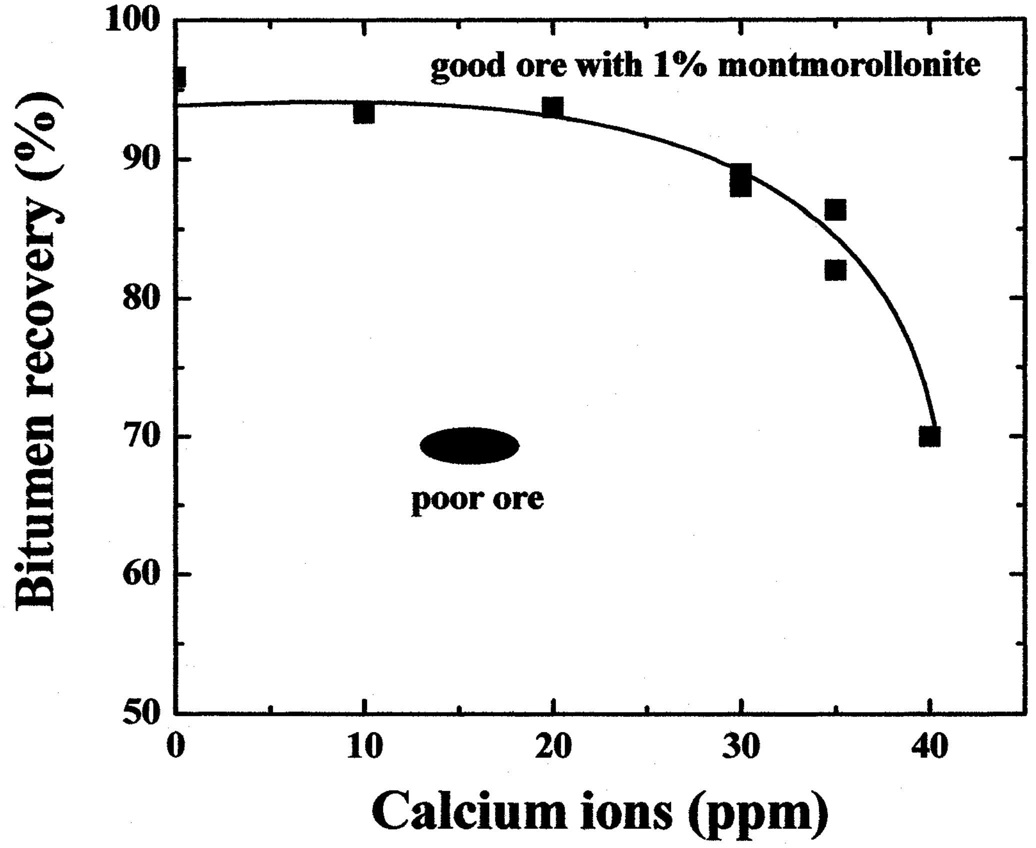


Figure 4-6: Effect of Ca ions concentrations and 1% montmorillonite clay doped to good processing oil sand ore on bitumen recovery in deionized water at 76°C and recovery of bitumen for poor processing ore sample

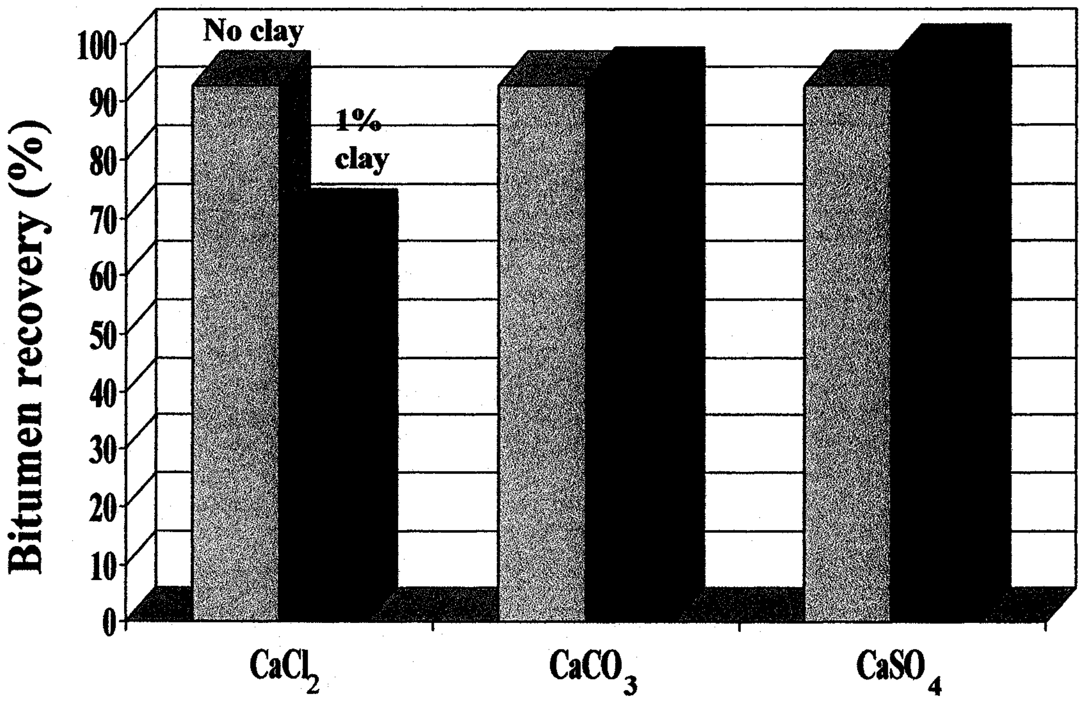


Figure 4-7: Effect of 40 ppm calcium from different sources of ions in deionized water at 76°C without and with 1% montmorillonite clay on bitumen recovery

gypsum $CaSO_4$. This finding suggests that decreasing calcium concentration in water would minimize depression of bitumen during flotation.

4.3.6 Effect of Divalent Cations and Clays on Bitumen Recoveries

Bitumen recovery decreases more drastically below 40% when 1% montmorillonite clay was mixed with 40 ppm magnesium compared to calcium as shown in Figure 4-8. It appears in Figure 4-9 that with 1% montmorillonite clay addition to an oil sand sample, increasing magnesium concentration in water is more detrimental than increasing calcium ions in depressing bitumen recovery as in Figure 4-10. However, the atomic weight of magnesium is smaller at 24.305 gr per mole compared to calcium that weights 40.08 gr per mole. A 40 ppm magnesium is equivalent to 1.6 mM, which is higher than 1 mM calcium at 40 ppm. Figure 4-11 shows that over a wider range in molar concentrations; mixing 1 wt% montmorillonite clay with the same molar concentration of either calcium or magnesium, have similar depressing action on bitumen recovery. This finding suggests that primary bitumen recovery is affected by the valence of the dissolved ions more than by the type of metal ions (Xu and Masliyah, 2001; Cuddy, 2000 and Wallace et al., 2001.

4.3.7 Effect of Divalent Cations (Mg^{2+} and/or Ca^{2+}) and changing Clays Concentration on Bitumen Recoveries and Froth Quality

The effect of increasing montmorillonite clay content from 0% to 1% of oil sand ore in the presence of 40 ppm Ca is shown in Figure 4-12 and in Figure 4-13 in presence of 40 ppm Mg. They show an increase of depression of bitumen recovery with the increase of clay content in the ores.

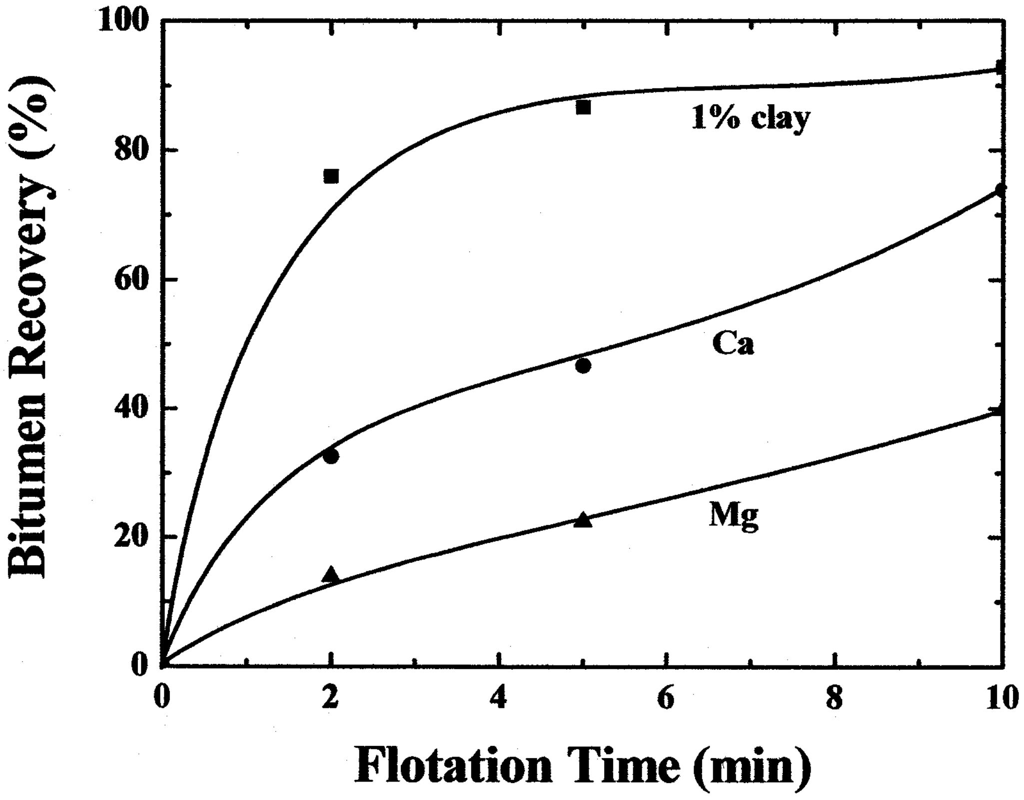


Figure 4-8: Effect of 40 ppm Ca and 40 ppm Mg additions on bitumen recovery in the presence of 1% montmorillonite clay doped to good processing oil sands ore samples in deionized water at 76°C

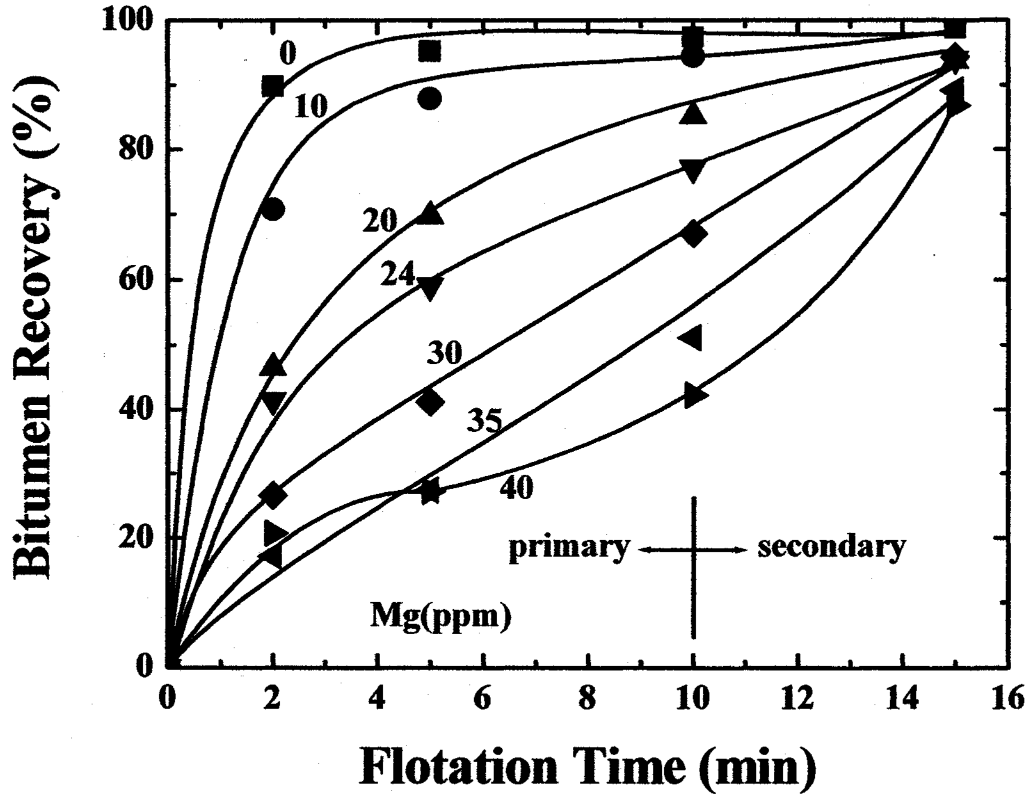


Figure 4-9: Effect of Mg^{2+} concentrations on bitumen recovery at pH 7.3 in the presence of 1% montmorillonite clay doped to good processing oil sands ore sample in deionized water at 76°C

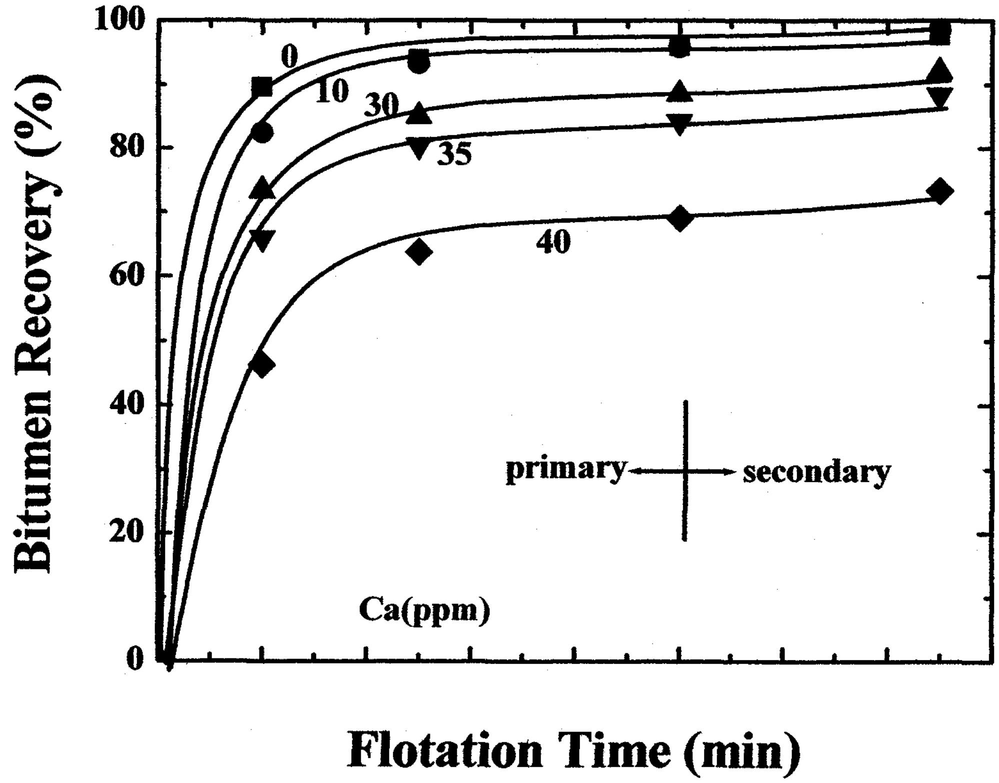


Figure 4-10: Effect of Ca^{2+} concentrations on bitumen recovery in the presence of 1% montmorillonite clay doped to good processing oil sands ore sample in deionized water at 76°C

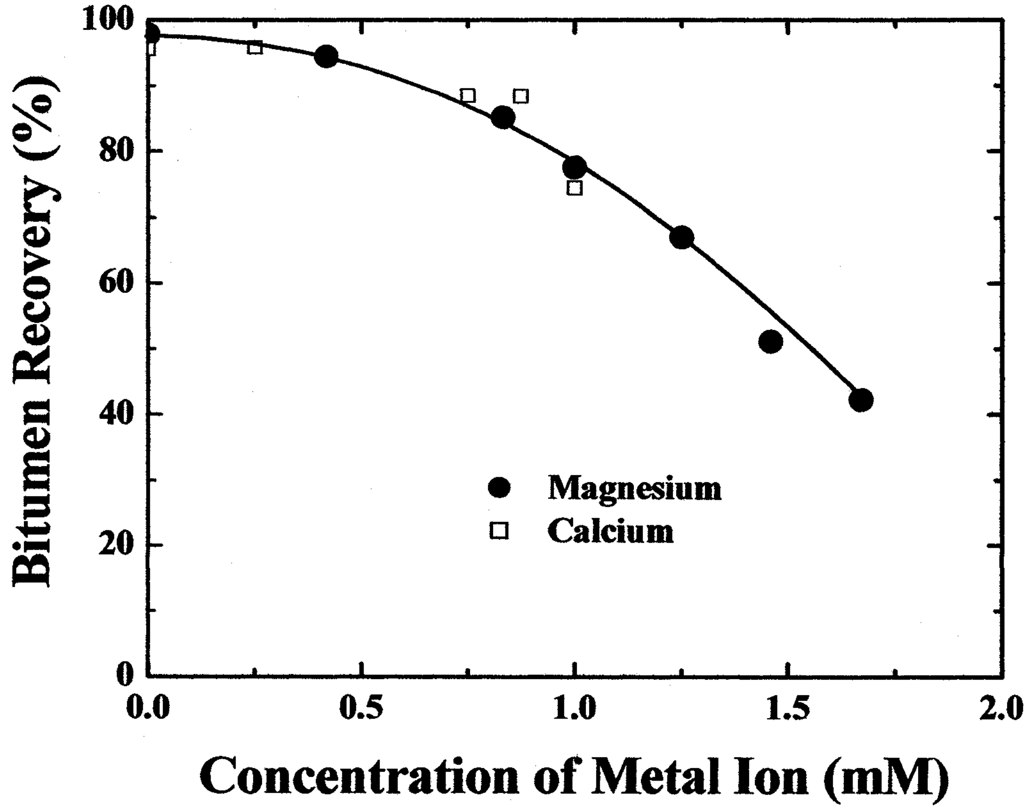


Figure 4-11: Effect of Ca and Mg ion additions expressed in molar concentration on bitumen recovery in the presence of 1% montmorillonite clay doped to good oil sand ores in deionized water at 76°C

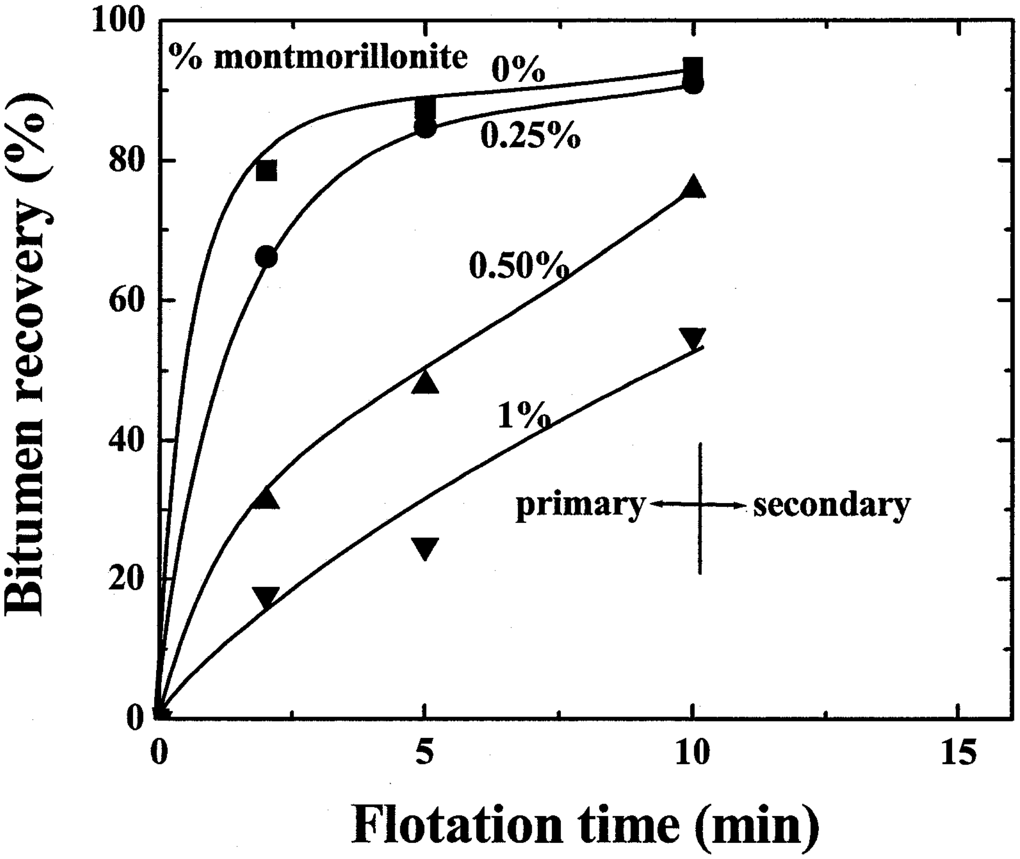


Figure 4-12: Effect of concentrations of montmorillonite clay addition in percent of good oil sand ore in deionized water containing 40 ppm Ca^{2+} at 76°C on bitumen recovery

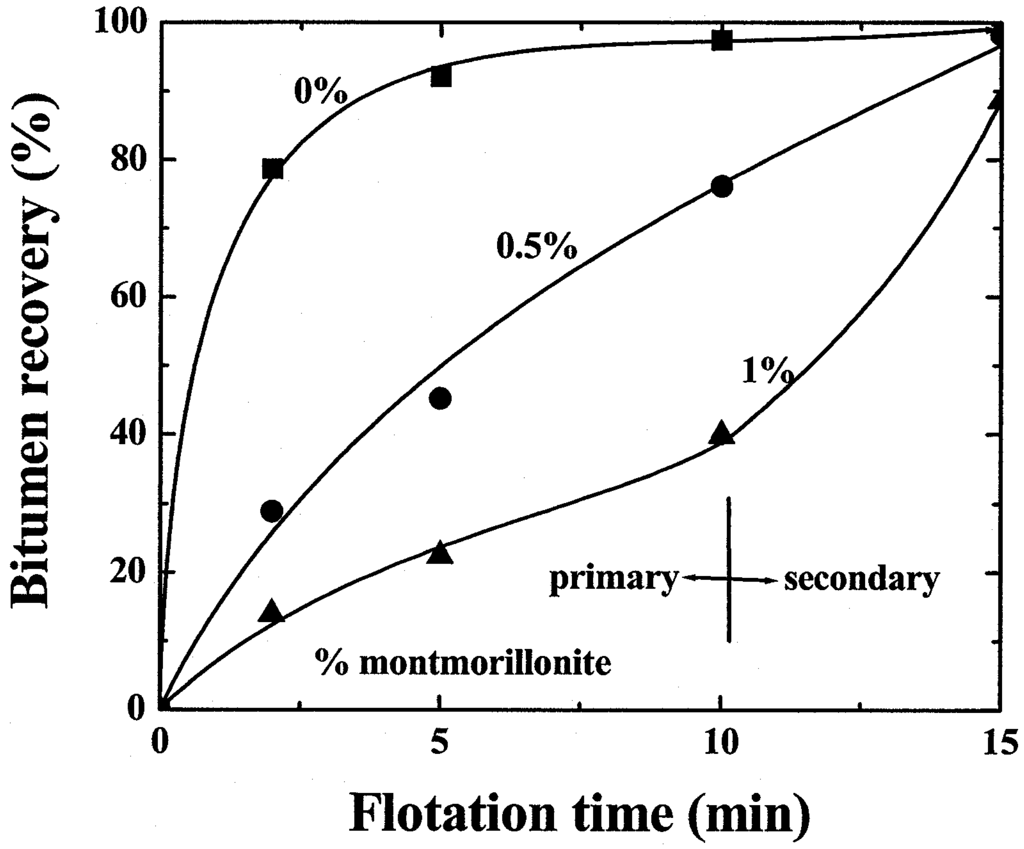


Figure 4-13: Effect of 40 ppm Mg^{2+} and variable concentrations of montmorillonite clay addition (in percent of oil sands ore sample) on bitumen recovery for good ore in deionized water at 76°C

4.3.8 Effect of Divalent Cations (Mg^{2+} and/or Ca^{2+}) and Clays on Froth Quality

Figure 4-14 shows that bitumen content of the froth also decreased from 42% bitumen without clay addition to 25% bitumen in the presence of calcium and to 18% bitumen in the presence of magnesium when 1% montmorillonite clay is added to the oil sand. The decrease of the froth quality is due to its dilution by fine clays, which entered froth either as slime coatings on bitumen surfaces or by entrainment in water and as result of flotation of surface modified clays. This finding suggests that with 40 ppm Mg or Ca ions in operating plants, the build up of montmorillonite clays in the slurries by recycling or from recycled water may depress bitumen recovery and reduce froth quality.

4.3.9 Effects of Caustic on Poor Processing Ore

After poisoning oil sands with 40 ppm calcium and 1% montmorillonite clay, the depressed bitumen recovery suggests that the bitumen surface is modified. Its original hydrophobicity in water does not recover even after we have washed the surface by immersing it in deionized water and being agitated at the conditioning temperature. This observation indicates that the slime coating is strongly attached to the bitumen surface to depress bitumen recovery, suggesting chemical binding of bitumen with clay. Therefore caustic has been the process aid of choice in the hot water extraction process to mitigate the depression of bitumen recovery (Dai, 1996) by changing the surface of bitumen in flotation, and then restoring depressed bitumen recovery. There is, however, an optimum dosage that varies around 0.04% by weight of oil sands, depending on the ore type and fines content (Sanford, 1983). We have chosen the same dosage of caustic for our

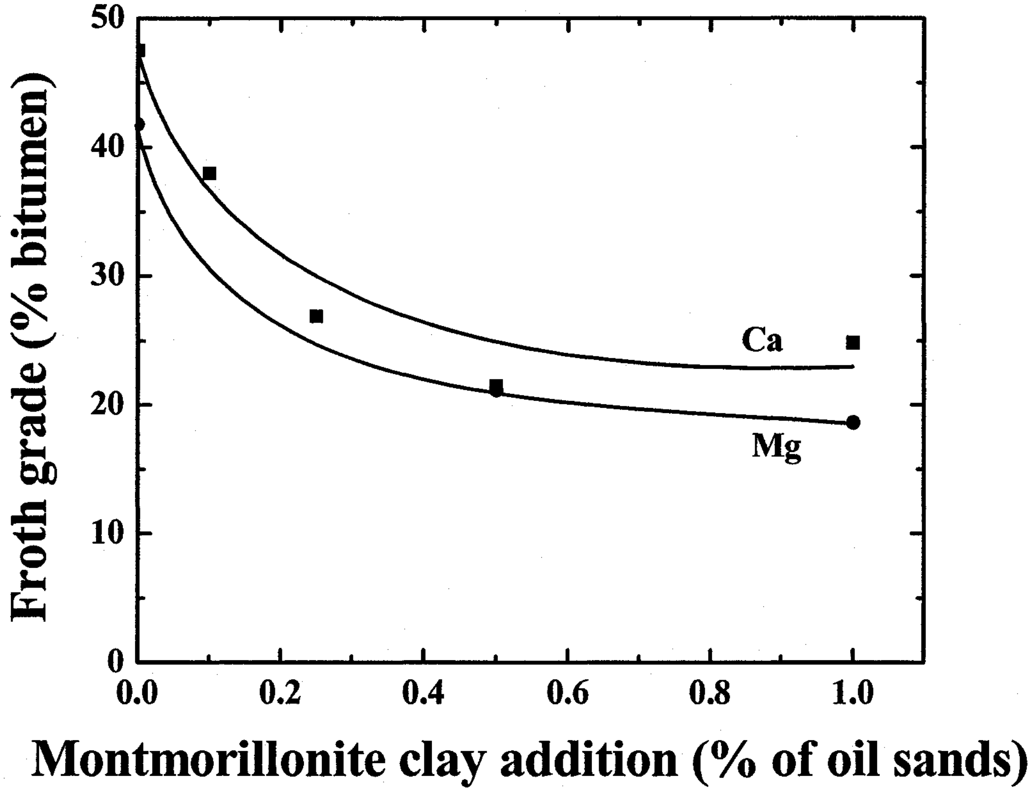


Figure 4-14: Effect of montmorillonite clay concentrations (percent of oil sands ore sample) on froth quality (percent bitumen) in the presence of 40 ppm metal ions for good ore in deionized water at 76°C

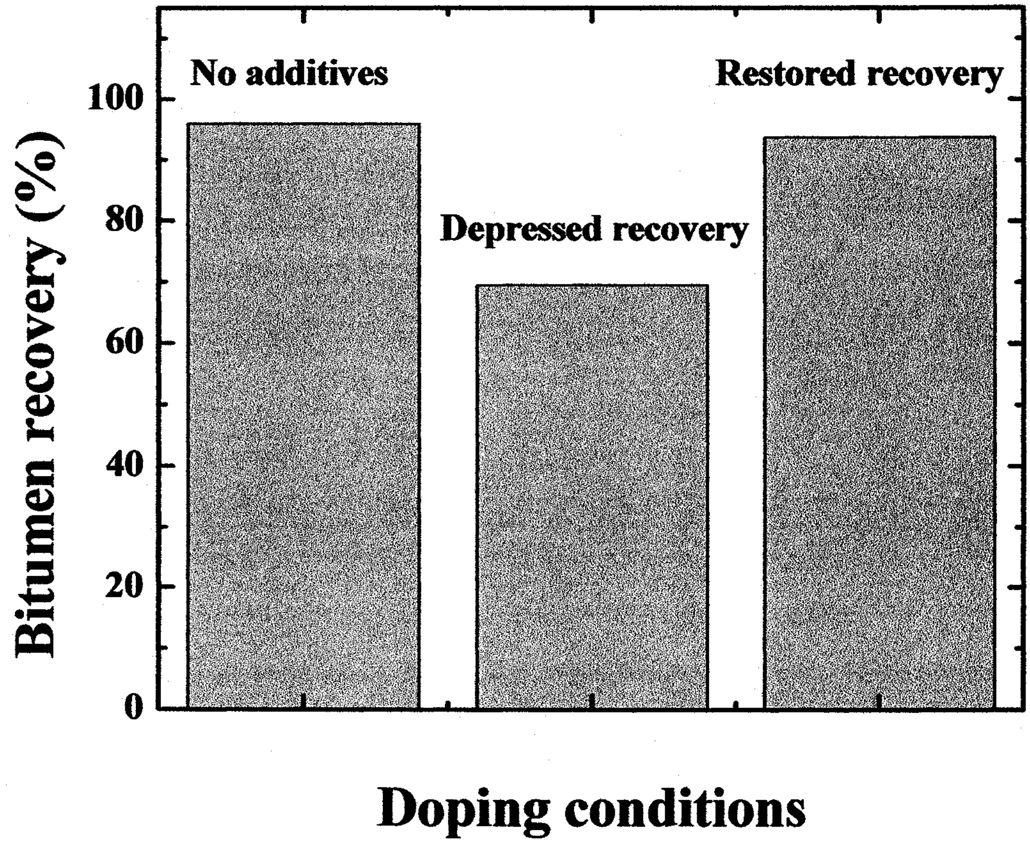


Figure 4-15: Effect of Ca ions (ppm) and of clays (% oil sands sample) doped to depress bitumen recovery at pH 7.7 from pH 7.3 in deionized water with no additives and effect of caustic (0.04 % oils sands ore sample) at pH 9.45 to restore depressed bitumen recovery for good processing ore at 76°C

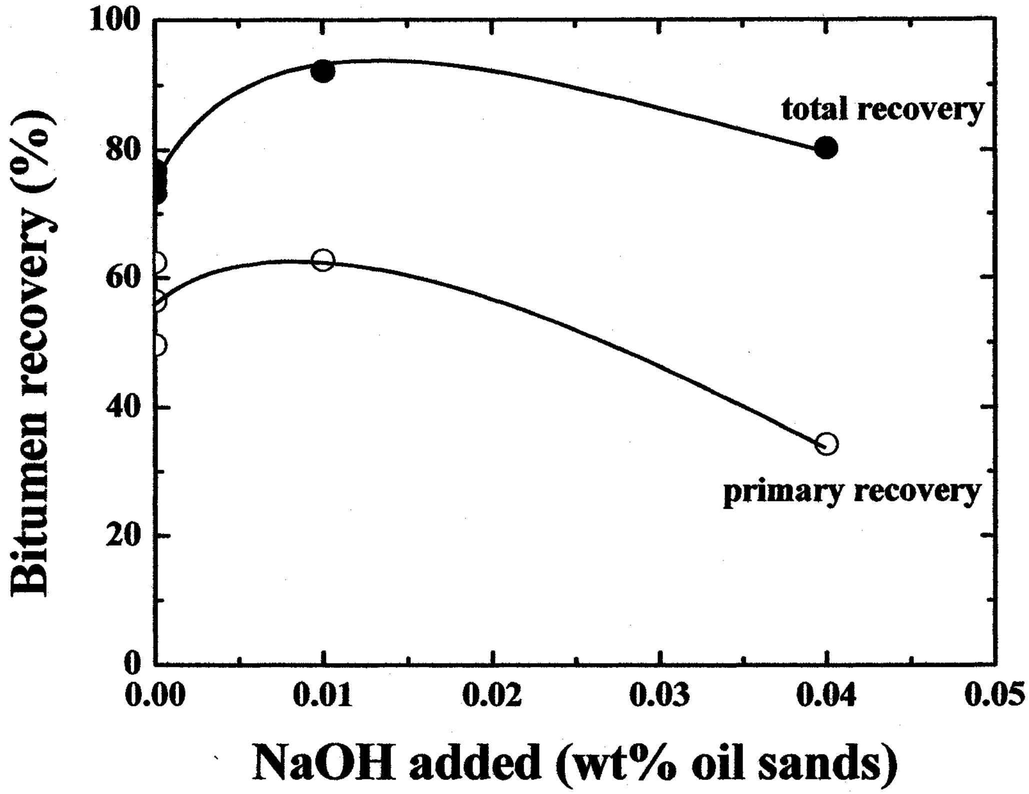


Figure 4-16: Effect of caustic addition to restore bitumen recovery for poor processing ore without additive in deionized water at 76°C and pH at (6.77-7.99)

flotation test to explore the effect of pH on the slime coating in restoring bitumen recovery. Natural pHs were in the range 6.77-7.99, they were measured but not modified. Caustic was added at the beginning of conditioning stage before poisoning, during conditioning when poisoning takes place and after conditioning but before the addition of flooding water when bitumen is fully poisoned. The results in Figure 4-15 show that the addition of caustic at 0.04% by weight of the good oil sand ore helped to maintain good processing conditions, it prevented depression during conditioning and it did help to restore the loss of bitumen recovery from its depressed low level back to its not depressed baseline level in the doping tests. The dosage of caustic addition to poor oil sand ore was selected as in the commercial plant practice at 0.01% and 0.04% by weight to study the potential to restore depressed bitumen recovery. Figure 4-16 shows that primary bitumen recovery is improved only by 3% with 0.01% caustic addition, which is much a less improvement compared with the case of poisoned good processing ores. A further increase in caustic addition to 0.04% depressed bitumen recovery. The results in this figure suggest that for different type of ores, test work is needed to find the level of caustic addition that improves bitumen recovery.

4.3.10 Effect of Bicarbonate as Process Aids

Sodium bicarbonate ($NaHCO_3$) addition made at different conditioning stages was also tested. We observed that when bicarbonate is added to water prior to conditioning, it increases pH; it softens water by precipitation of calcium based on the following reaction:

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3$$

The softening of process water improves bitumen recovery by avoiding depression, leading to an even slightly better recovery than the baseline results as shown in Figure 4-17. However the addition of sodium bicarbonate after bitumen was fully depressed showed only a marginal improvement in restoring bitumen recovery from depression.

In a case study, samples from Albian Sands Energy Inc. were floated using the Athabasca River water and the basal aquifer water that is richer in bicarbonate. The results in Figure 4-18 shows that the bitumen recovery was improved only marginally with increasing the basal water addition to the Athabasca River water before flotation.

4.3.11. Effect of Circulating Loads of Fines

The effect of diluting fresh good processing ore feed sample containing low fines by adding an increasing amount of fines was studied by adopting locked cycle test procedures developed originally for base metal flotation tests. In this case, two samples of poor processing ores were processed to produce tails water and sufficient solid particles that were screened to pass 325 mesh screen (- 44 microns). Appropriate amounts of recovered water and fines are mixed with the good processing ore sample for flotation. The amount of good processing ore was reduced by the increase of fines, diluting the feed grade from 10.57% high grade bitumen range to below 8.9% bitumen that is characterized as medium grade ore (Figure 1-4). Figure 4-19 shows that compared with the baseline conditions shown by the upper curve (10.57% bitumen), primary bitumen recovery is depressed significantly from 95% to 85% when good processing ore was doped with 15% fines from poor processing ores or with 15% kaolinite clay addition.

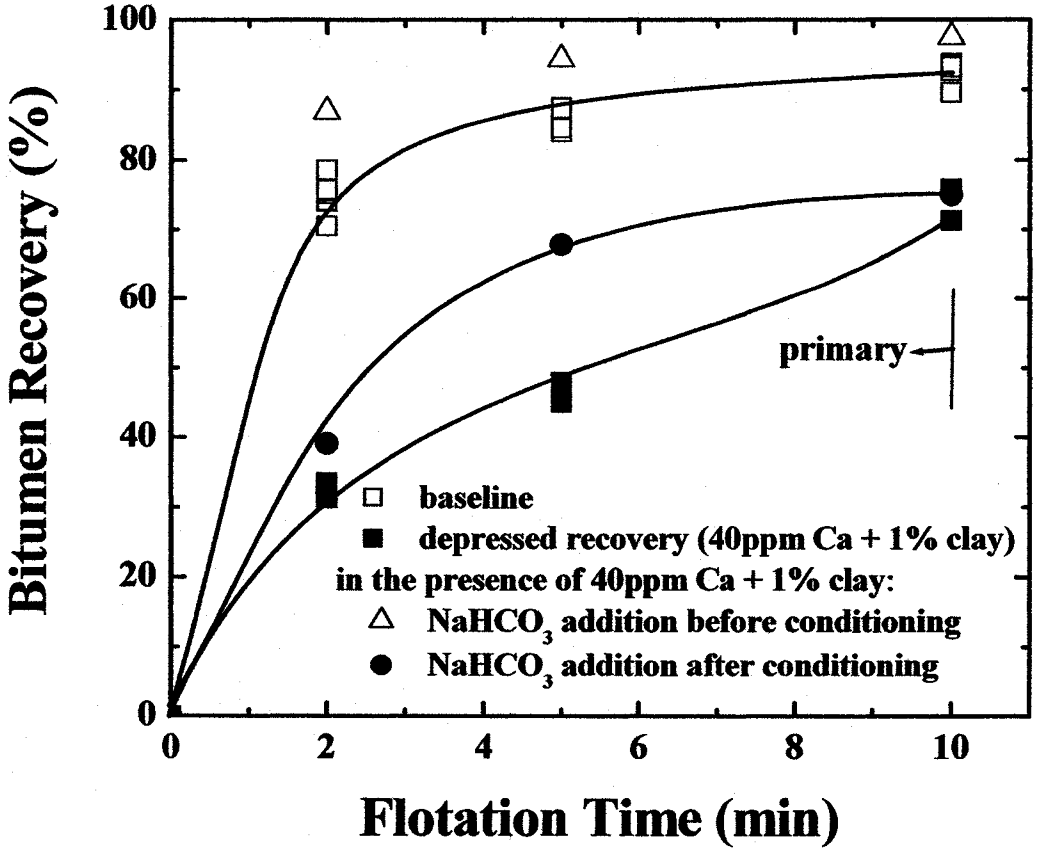


Figure 4-17: Effect of addition of sodium bicarbonate (1000 ppm) at pH 9.3 on bitumen recovery in the presence of depressing conditions of good processing ore by 40 ppm calcium ions and 1% montmorillonite clay in deionized water at 76°C

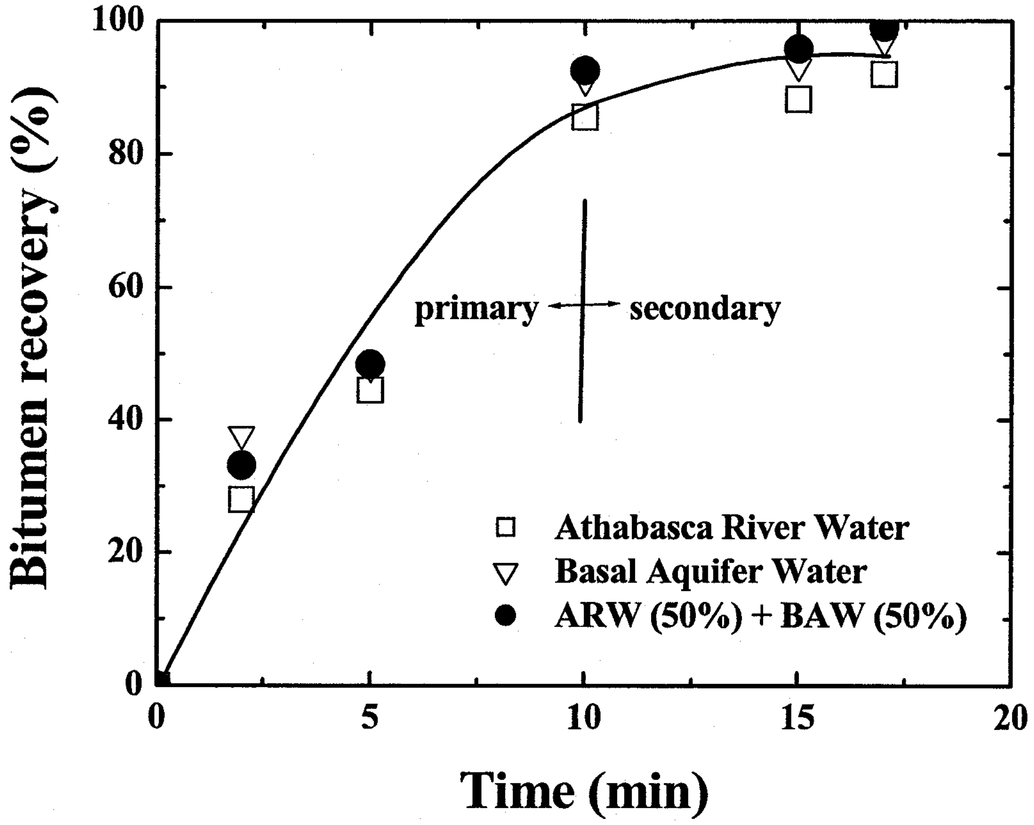


Figure 4-18: Effect of different water types on bitumen recovery for good processing ore from Albian Sands Energy Inc. at 76°C

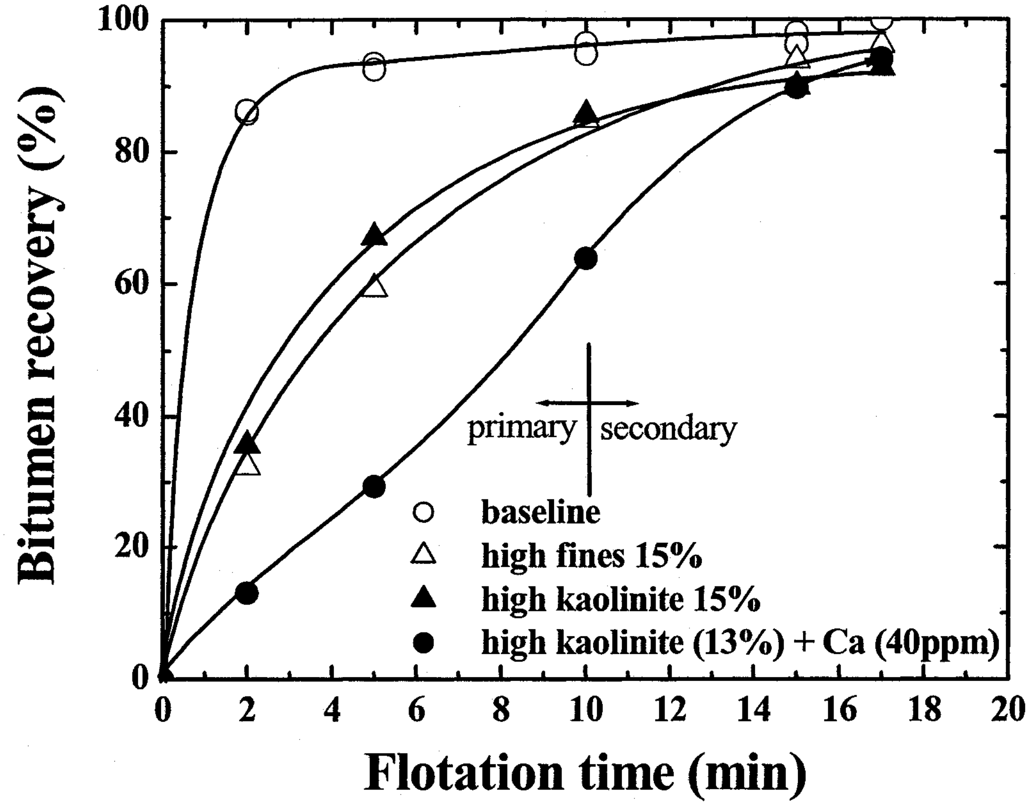


Figure 4-19: Effect of high fines (15% of the oil sand) from flotation of poor ore and of high kaolinite (15%) doped to good processing ore sample in the absence of calcium compared to the effect of high kaolinite (13%) in the presence of calcium (40ppm) on bitumen recovery at 76°C

More severe depression from 95% to 63.8% primary bitumen recovery was observed when good processing ore was doped with 13% kaolinite clay and 40 ppm calcium ions. This depression of primary bitumen recovery compares with poor processability of low grade ore shown in Figure 4-20. These findings suggest that increasing fines contents indistinctly dilute samples from good processing high grade ore into poor processing low grade ore, shifting good bitumen recovery to increasing depressed bitumen recovery. The effect of recycled fines is experienced in commercial operations by the Albian Sands extraction operations where the high fines content froths from primary and secondary flotation, and high fine thickener overflow used as dilution water are recycled to the PSC feed. They force the operations to reduce the fresh feed throughput, dilute the PSC feed grade and enhance depression of bitumen recovery of the LEE process.

4.3.12 Effect of Feed Ore Grades on Bitumen Recovery

Oil sands ore samples with a wide range of bitumen grades (6.05% - 14.88%), shown in Table 3-1, were tested in our study. Although oil sands ore with high bitumen content are often considered to be good processing ores, we found in our laboratory tests lower primary bitumen recoveries and slower kinetics for some higher grade ore samples containing 12.8-13.6 % bitumen, in contrast to higher primary bitumen recoveries for lower grade ore samples containing 10.3-10.74 % bitumen, as shown in Figure 4-21. Crickmore et al. (1983) and Schramm (1985) earlier detected a similar trend of poorer bitumen recovery from ore samples with higher bitumen content. This observation seems to be in contradiction with the expected behavior of oil sands ores that features that at a given processing condition, high grade ores (low fines) feature a higher baseline bitumen recovery than low grade ores (high fines) (Kasperski, 2001). The apparent inconsistency

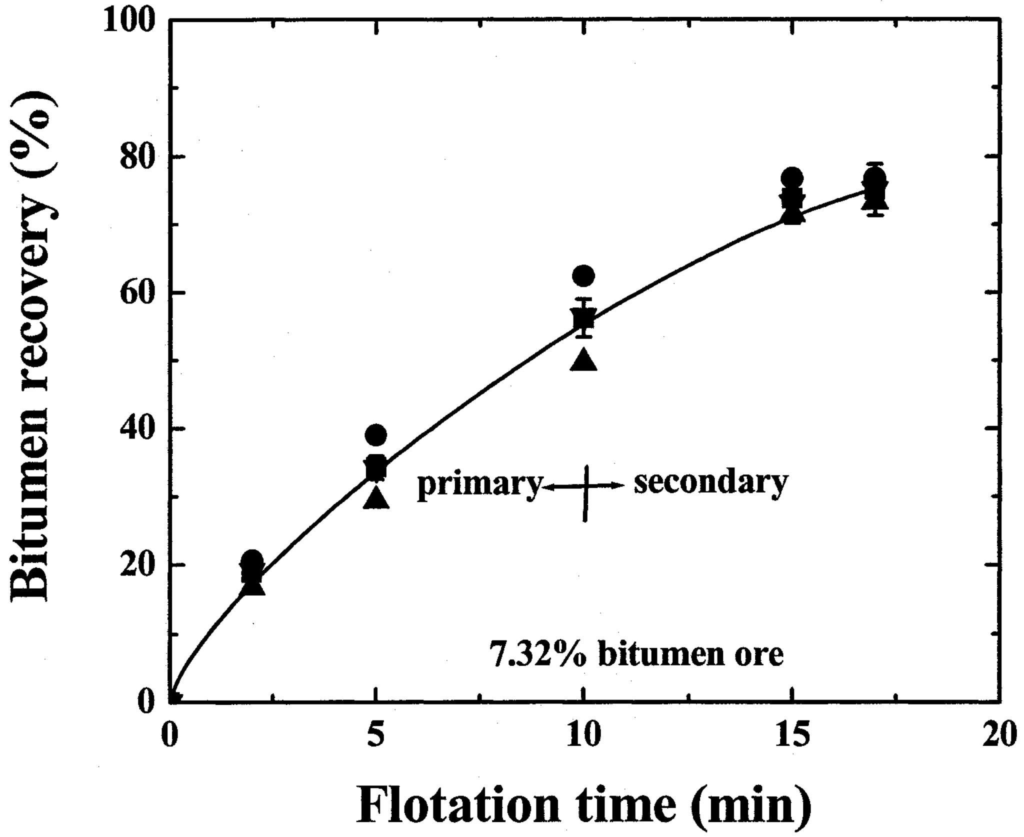


Figure 4-20: Bitumen recovery for poor processing ores in deionized water at 76°C

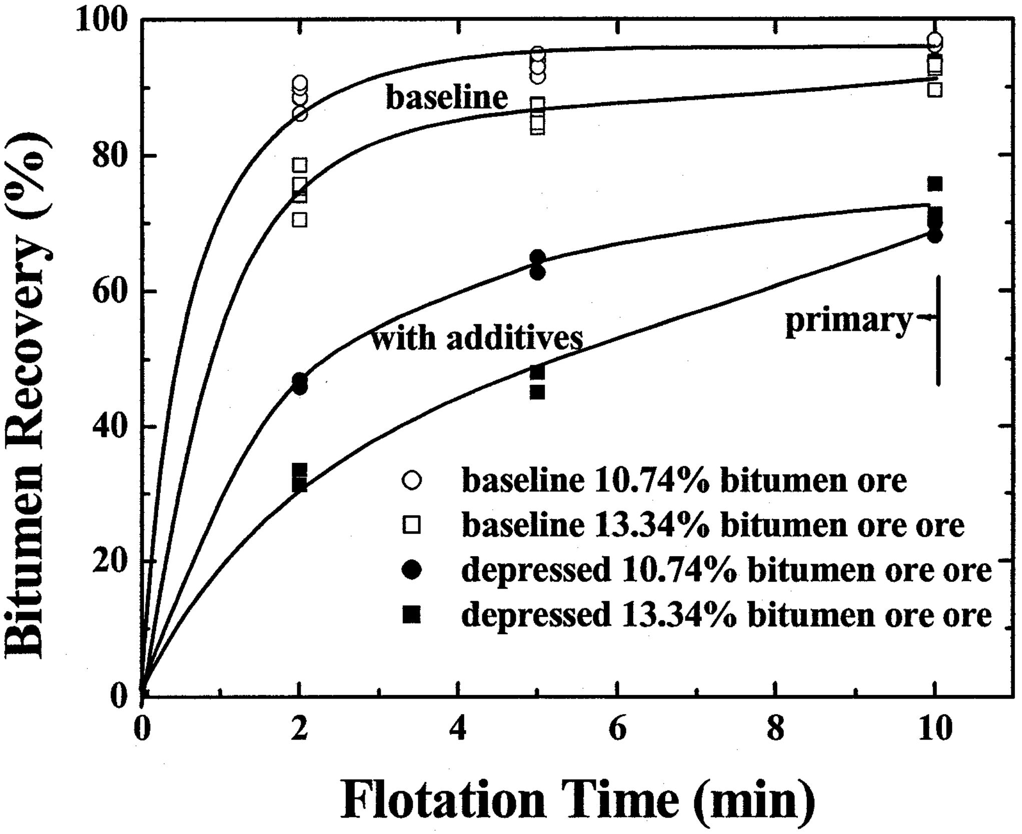


Figure 4-21: Effect of changes in ore grades (old ore at 10.74% versus new ore at 13.34%) and in additives (calcium ions and montmorillonite clay) on bitumen recovery at 76°C in deionized water

implies that using bitumen content as a marker must use extreme caution in assessing processability of oil sands ores.

4.3.13 Effect of Mechanical Energy Input by Agitation

The impact of mechanical energy and high shear during conditioning and flotation stages were studied for poorly processing ore samples by changing agitation rates of stators in Denver cell from 1200 rpm to 1800 rpm. This effect would affect ablation, ore digestion and bitumen liberation (Malmberg, 1968). The results in Figure 4-22 show that at 1200 rpm, the primary bitumen recovery is only 59.5 %, in comparison to 85.8 % at 1800 rpm for the ore sample tested. This observation suggests that an increase in energy input improves bitumen recovery. However an excessive energy input would slurry clays and increase its contents into the froths. Insufficient energy input, on the other hand would lead to poor bitumen recovery. Sanford (1983) proposed a gentle shear condition that separates bitumen from sand grains without excessive fragmentation of bitumen into small droplets that are difficult to float. Thus, for bitumen extraction tests using a laboratory Denver cell, it is important to determine the optimum energy input so that a high bitumen recovery and good froth quality could be achieved during the slurring step.

4.4 Visualization Studies

4.4.1 Bubble formation, Visualization of the Air Bubbles Size and Application.

The change of bitumen hydrophobicity, seen in chapter 2, involves the presence of air bubbles for the attachment to occur. Air is entrained or is mechanically blown into the slurry. Bitumen recovery will depend on the amount of attached bitumen that is provided

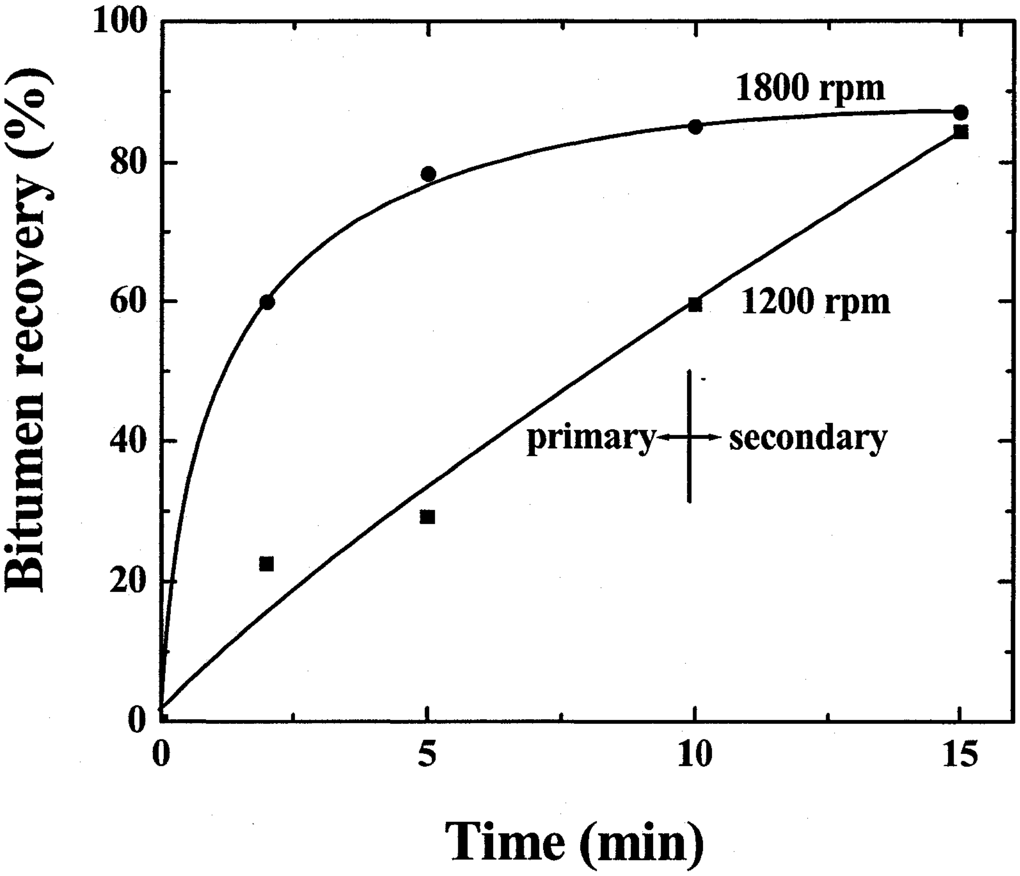
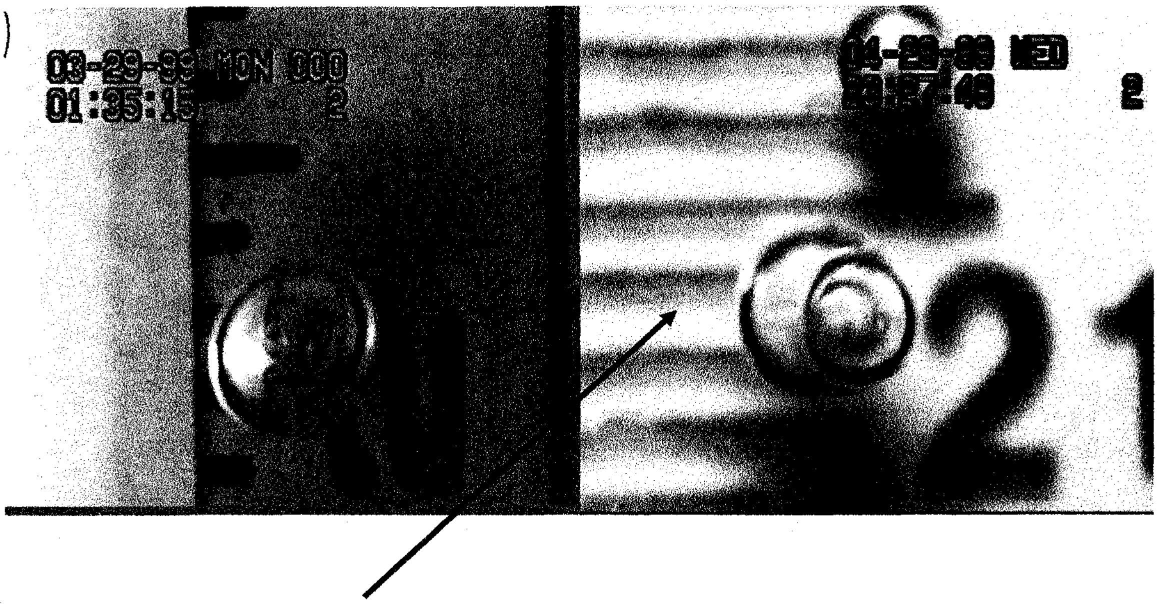


Figure 4-22: Effect of energy by increasing the agitation rate (RPM) using deionized water on bitumen recovery for poor processing ores sample (7.9% bitumen) at 76°C at pH 7.13

by the availability of air bubble surface area, and on the strength of air bubble-bitumen attachment to resist separation during the rise of the aggregates to the froth zone. A given volume of air will have more surface area if air is finely divided into small air bubbles that are more dispersed in the slurry (Gaudin, 1957). Small air bubbles have slow rising velocity that increases the retention time into the slurry and allows the increase of bitumen loading to take place and be carried to the froth zone. It is then important to visualize how operating conditions will affect bitumen recovery loading the air bubbles. Figure 4-23 shows a few clear air bubbles generated in de-ionized water. The diameter of air bubbles is generally bigger than 2 mm. The shape is typically not spherical and the rising velocity is so high that bubbles don't appear on two consecutive frames, making it difficult to determine the rising velocity. As pure water does not foam, the frother Methyl Isobutyl Carbinol (MIBC), from Dow Chemicals, is commonly used in mineral flotation to generate smaller bubbles and make stable froth. In this study, MIBC was used as received and dropped into water using a micro syringe to a concentration around 1-2 microlitre per liter (ppm). The air addition is kept low to minimize coalescence and to differentiate a wide size range of air bubbles.

As shown in Figure 4-24, the air bubbles generated in MIBC are much smaller and more spherical in shape than those in "pure" de-ionized water. Their sizes range between 0.2 to 1mm. We have centrifuged the process water collected from flotation of bitumen from good processing ores. It was left still to remove solids by decantation. Surfactants released during flotation adsorb preferentially at the water-air interface and they enhance generation of fine bubbles as seen in Figure 4-25. They stabilize the froths so that water



Scale 1 mm

Figure 4-23: Air bubbles in deionized water at 76°C

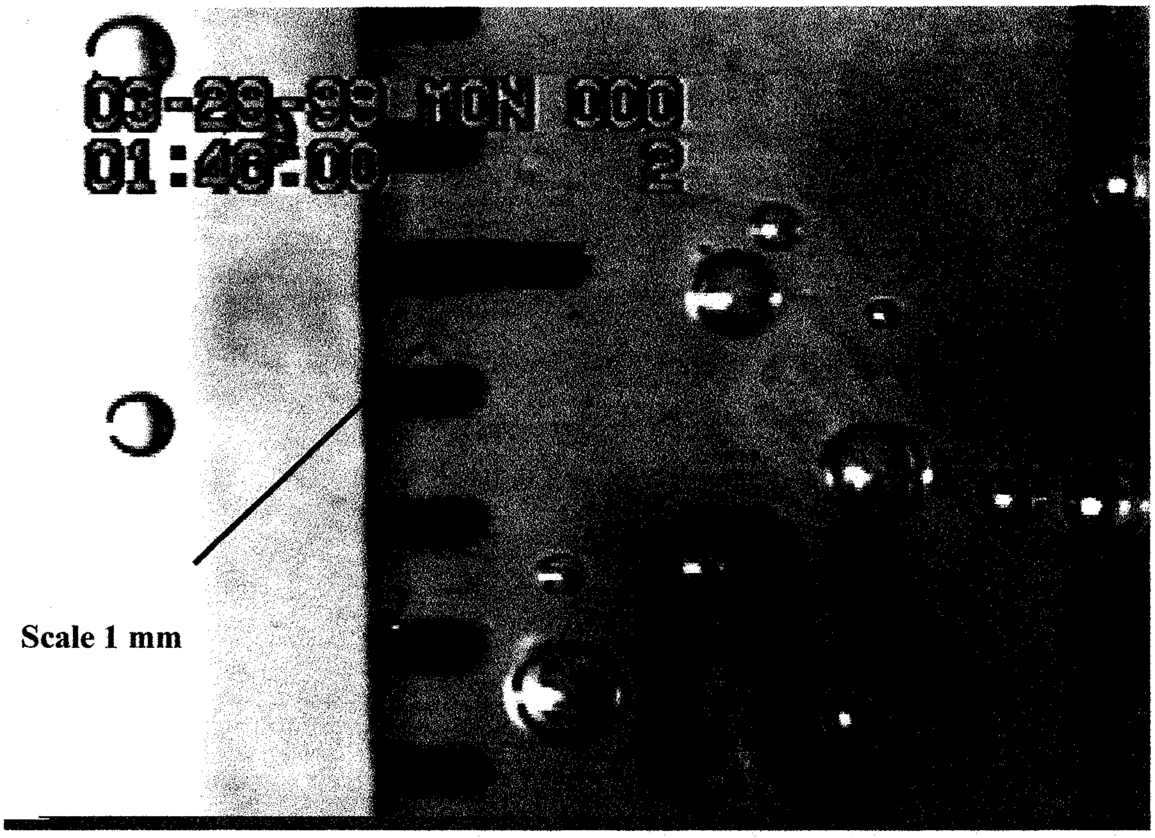


Figure 4-24: Air bubbles formed in deionized water containing 1-2 ppm MIBC at 76°C

Scale 1 mm

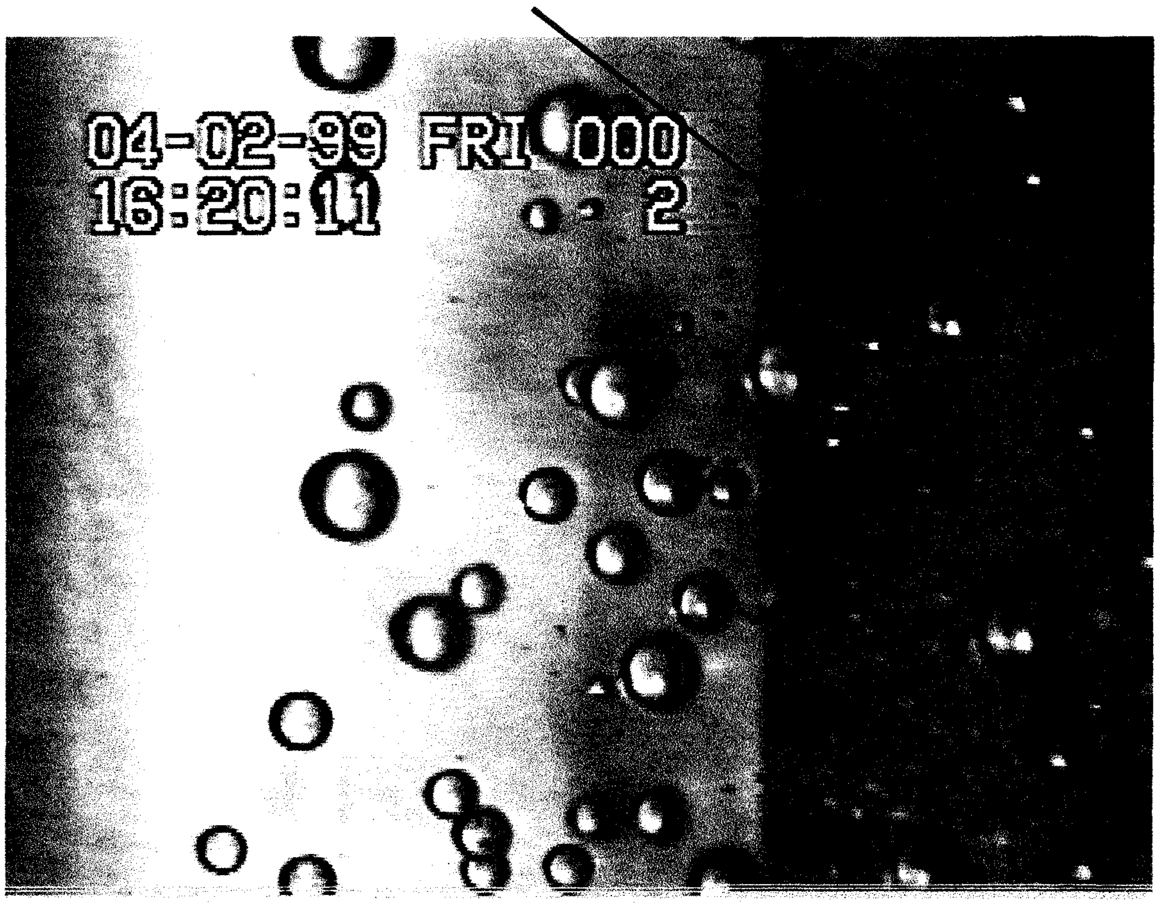


Figure 4-25: Air bubbles formed at 76°C in processed water containing natural surfactants released from bitumen flotation of good processing ore sample at 76°C

with small air bubbles will start to foam.

The visualization technique has helped to detect similarity in the reduction of air bubble sizes due to the addition of frother MIBC in Figure 4-24 and in the presence of natural surfactants in Figure 4-25. Air bubbles are small; they have spherical shape and have a similar size range. This observation suggests that the addition of the frother MIBC would not bring any improvement to the process compared with the effect of natural surfactants released by the good processing oil sand ores. The application of the finding has prevented the injection of frother at Albian Sands, resulting in substantial cost savings for the Low Energy Extraction Processes (LEE Process) at Albian Sands operations (Kasongo, 2002) and at Syncrude Aurora Project.

4.4.2 Bitumen loading patterns of Air Bubbles in flotation

Complete bitumen loading on an air bubble is beneficial for full utilization of air bubbles in flotation, as shown in Figure 4-26. This suggests that the density, ρ_a, of air-bitumen aggregates is lower than the density of water ρ_w. In this case, $\Delta\rho$, the density difference (ρ_a - ρ_w) between the aggregate and water, is negative. With 'a' being the aggregate radius, and g the gravitational acceleration (m/s^2), the aggregate is under gravity force:

$$F = a^3 g \Delta\rho \qquad (4\text{-}2)$$

This force is negative and will contribute to the increase of the rising velocity of the aggregates to the froth zone (Masliyah, 2003). But even for good processing ores,

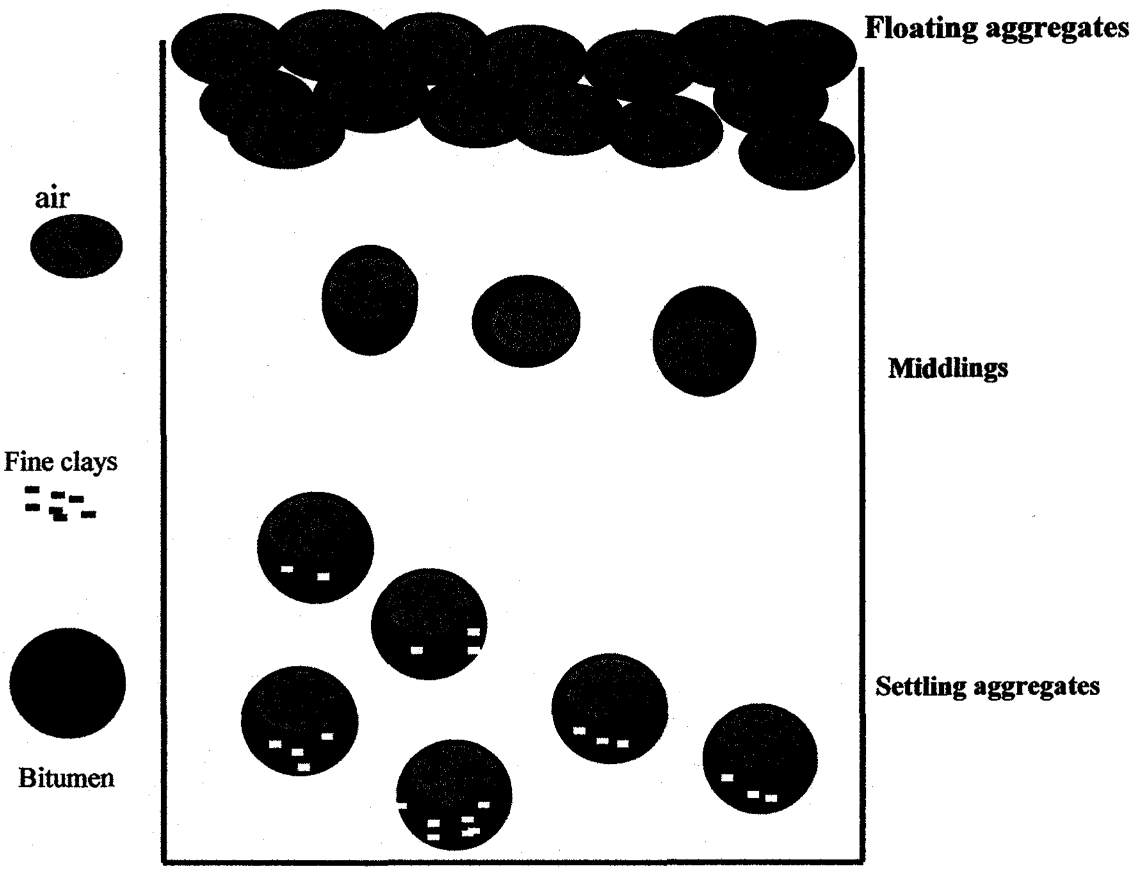


Figure 4-26: Schematics of bitumen loss by settling because of overloading with solid particles

bitumen droplets in real systems will acquire an higher density than water depending on the amount of solids that are attached to them (Bensebaa, 2000; Darcovich, 1989; Kotlyar, 1987a-b, 1988). In this case, $\Delta\rho$ becomes positive, and the gravitational force in equation 4.2 will oppose the rising of the aggregates to the froth zone.

A schematics of the bitumen loss mechanism, in Figure 4-26 shows how overloading air bubble-bitumen aggregate with solids will determine whether a bitumen droplet will be collected in the froth or settle and report to the tailing streams. Our visualization method provides this evidence in Figure 4-27, for the first time in oil sands, suggesting that there is an optimum range of relative size and amount of bitumen that can be loaded on the surface of air bubbles in the slurry for a maximum flotation recovery (Finch, 1990; Zhou, 2000). It appears that the froth underwash would help to release solids from froths to improve froth quality.

4.4.3 Effect of Temperature

The visualization study shows in Figures 4-28, grabbed pictures of bitumen flotation during conditioning under baseline conditions at 76°C and at 25°C. They allow for studying the effects of temperature change on the attachment of air bubbles to bitumen that impacts bitumen recovery. Figure 4-28(A) shows engulfment at a high temperature of 76°C when bitumen has a low viscosity. A dark and heavy load of bitumen suggests strong attachment of bitumen to air bubbles. This confirms that during the Clark Hot Water Extraction Process, bitumen will spontaneously attach to the air bubbles, spreading

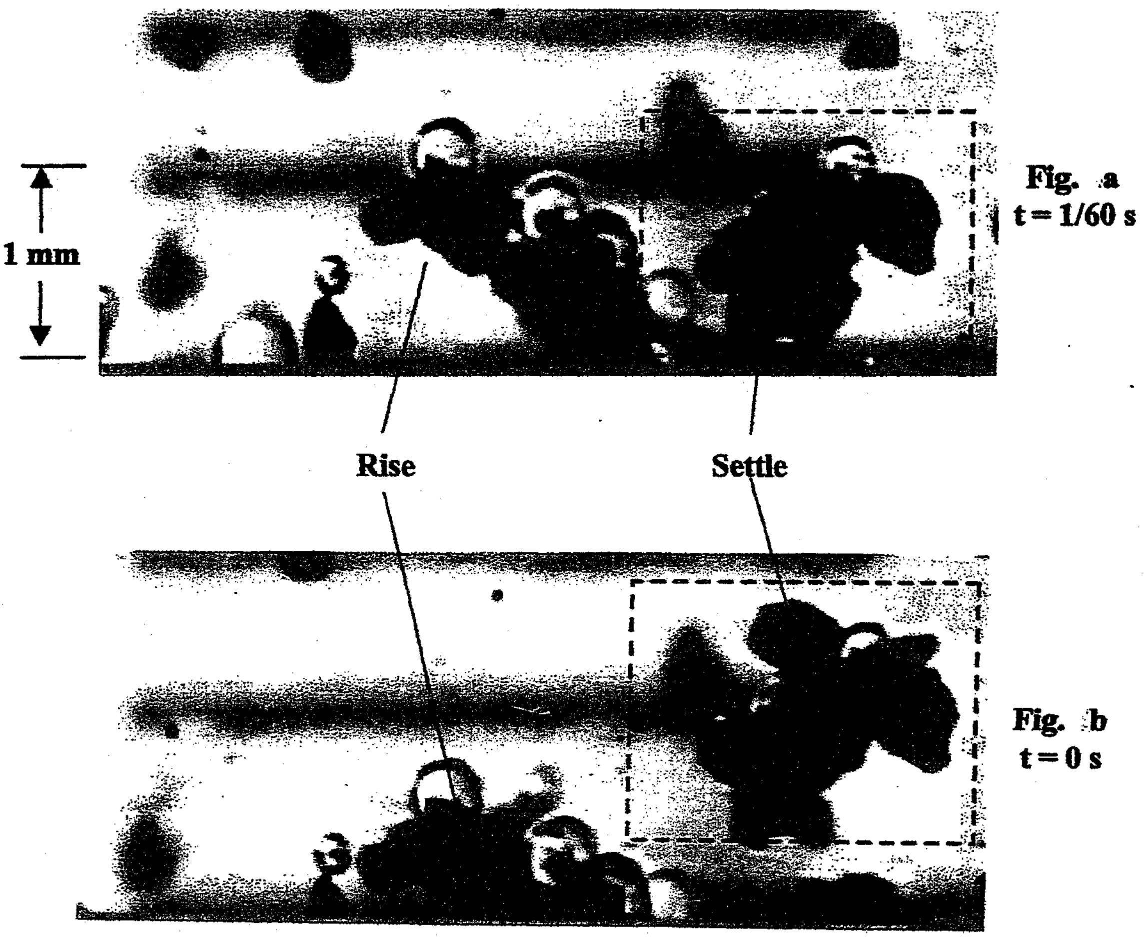


Figure 4-27: Settling of aggregates air bubble-coal due to overloading after Zhou et al. (2000)

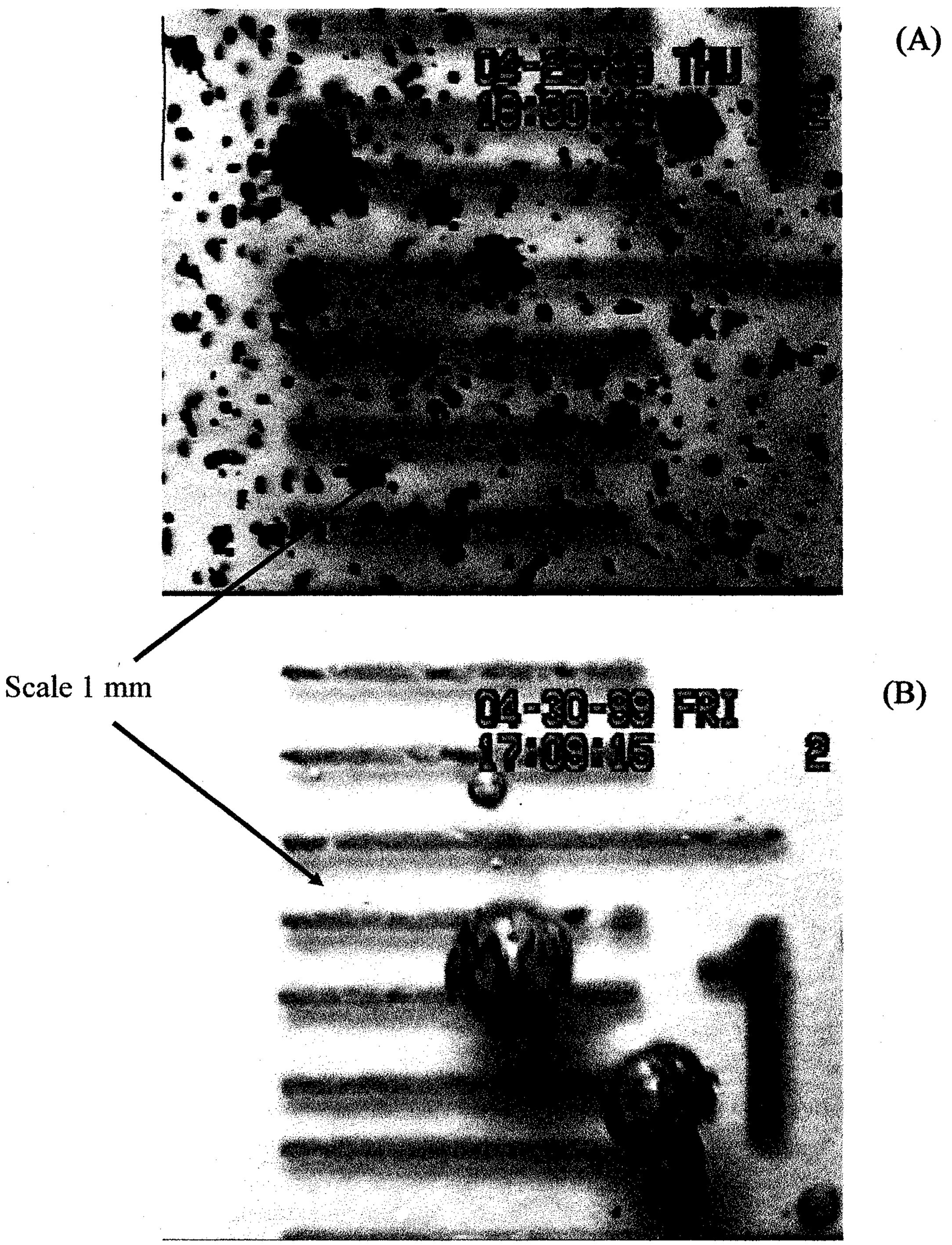


Figure 4-28: Effect of temperature: (A) Bitumen engulfing air bubbles at high temperature; (B) Bitumen hanging on air bubbles surface at room temperature during flotation in deionized water without additives

and engulfing the bubble surface resulting in high bitumen recovery and good froth quality. Figure 4-28(B) shows pictures at room temperature (25°C) when bitumen stays as viscous droplets that behave as solid particles. They attach by hanging to air bubbles and some free areas on the surface of the air bubbles are observed indicating that the air bubbles are not totally loaded. These findings suggest weak attachment of bitumen droplets to air bubbles at room temperature.

We have studied the effect of temperature on bitumen recovery using tap water at 25°C, 50°C, and 75°C. Results in Figure 4-29 show that bitumen recovery is higher at the higher processing temperature of 75°C. It decreases only marginally when temperature is decreased to 50°C. This finding suggests that bitumen recovery is less sensitive to temperature changes between 75°C-50°C. However bitumen recovery kinetics is affected drastically by a temperature decrease from 50°C to 25°C. Similar effects were reported in the literature (Kasperski, 2001; Innes, 1967; Bichard, 1987). The froth quality is characterized by its bitumen to solid ratio as shown in Figure 4-30 for the samples of ore treated suggesting a favorable increase at low temperature of 25°C over time compared to higher temperatures of 50°C and 75°C. The water contents shown in Figure 4-31 was found to be entrained more at high temperatures (50-75)°C than at 25°C.

This finding suggests that 50°C would be a sufficient and economic temperature level for maximum bitumen recovery by flotation; but care must be taken to improve froth quality by say froth underwashing operation. In this case, a stream of hot water sprays into the separation vessel to wash the entrained fine particles down to the middling zone or tails

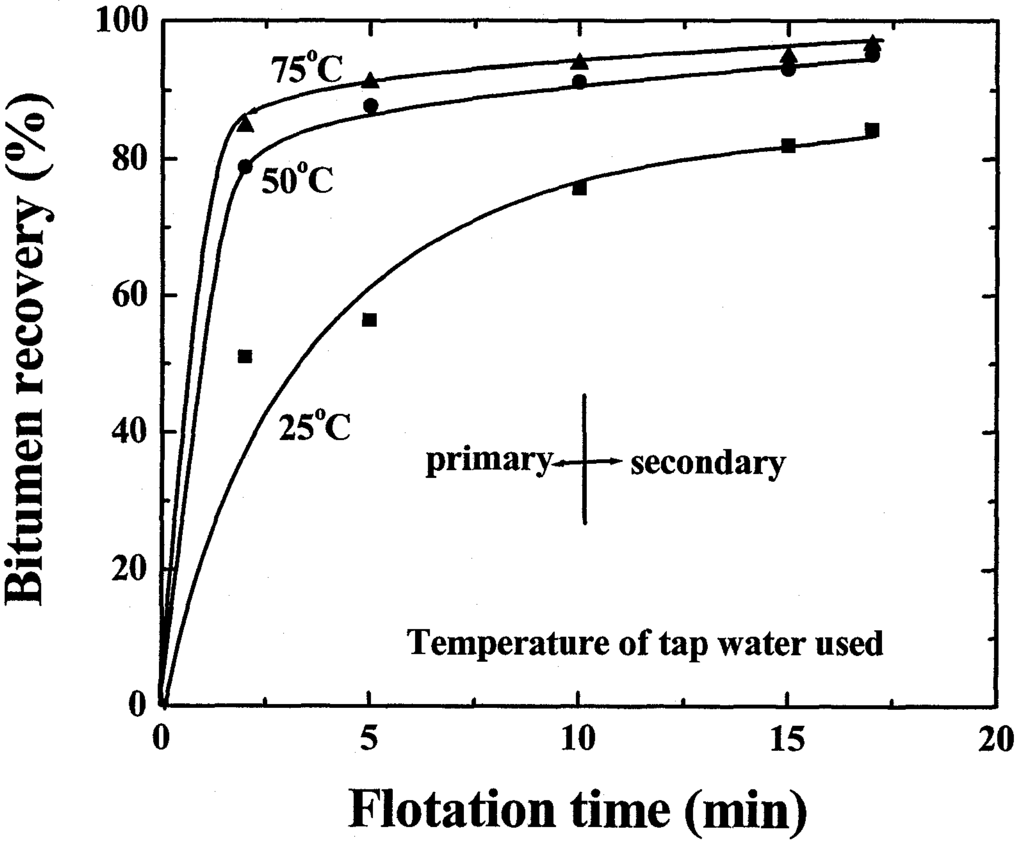


Figure 4-29: Effect of temperature on bitumen recovery using tap water without additives

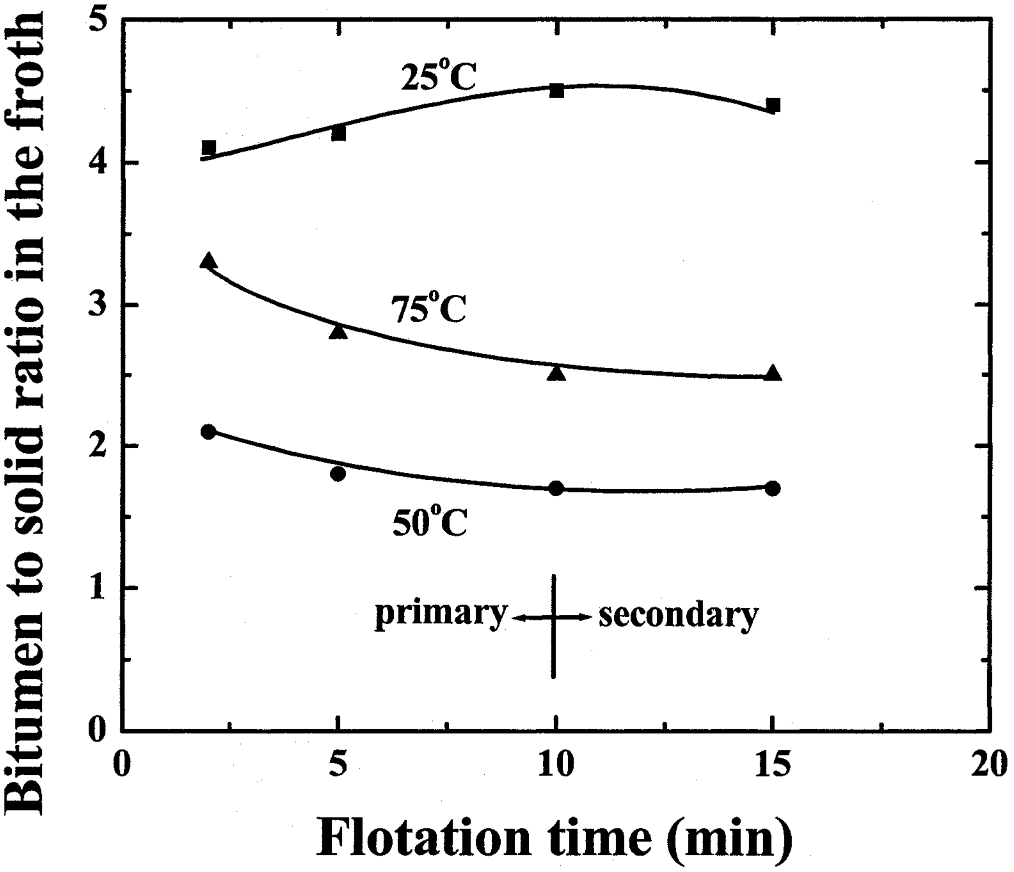


Figure 4-30: Effect of temperature on froth quality during flotation in deionized water on good processing ores

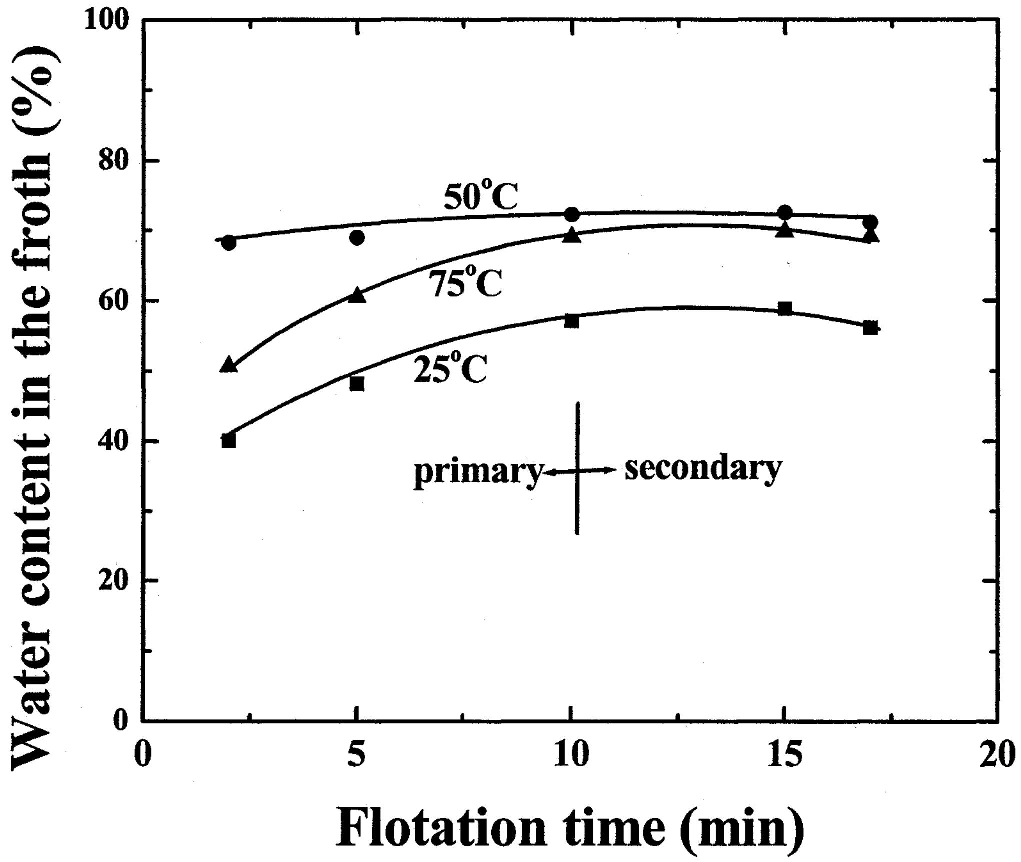
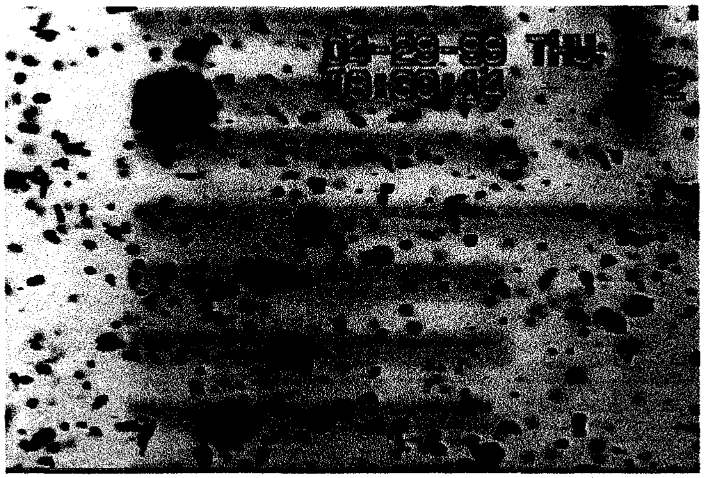


Figure 4-31: Effect of temperature on froth water content during flotation of good processing ore using deionized water

zone while bitumen loaded bubbles rise to the froth zone. Below 50°C, the OSLO Low Energy Extraction processes are viable if a sufficient conditioning time in hydro pipelines is ensured to correct this identified negative effect of the decrease of temperature on depression of bitumen recovery.

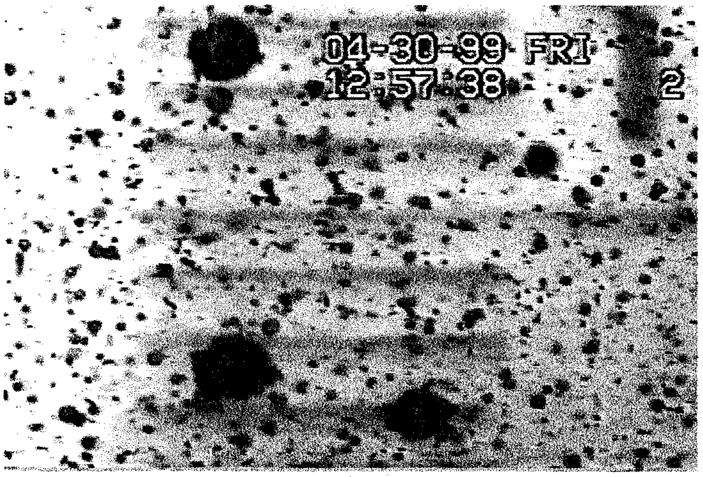
4.4.4 Effect of Fine Clays and Divalent Ions

Visualization of air bubbles in the slurry during conditioning is seen in Figures 4-32. These figures show the effect of metal ions and clays on bitumen recoveries. Figure 4-32a shows an image of good processing ore under baseline flotation conditions without additives. Air bubbles are dark and heavily loaded with bitumen with less bitumen left free in the slurry. This is an indication of strong attachment of bitumen to the air bubbles, resulting in a high bitumen recovery. Figure 4-32b shows an image of poorly processing ore under baseline conditions without additives. Air bubbles provide enough surface area, but they are light and less loaded with bitumen, with a large number of air bubbles left free from being covered by bitumen. This is an indication of weak attachment of bitumen to the air bubbles, resulting in lower bitumen recovery. Figure 4-32c shows an image of good processing ore that is doped with 1% montmorillonite clay and processed with 40 ppm calcium ions addition in deionized feed water. In this case air bubbles are spongingly loaded with bitumen and their appearance is similar to the poor processing ore in Figure 4-32b. This illustrates qualitatively and conclusively the detrimental effect of doping good processing ores with calcium and montmorillonite clay. This visualization technique gives direct evidence that surface hydrophobicity is a key characteristic for



(a): Good ore without additives at 76°C

(b): Poor ore without additives at 76°C



(c): Good ore with 40 ppm Ca and 1% montmorillonite clay addition at 76°C

Figure 4-32: Images of loading of bitumen on rising bubbles in Denver cell bitumen attachment to sustain the drainage of down-flow liquid during rising of air bubble-bitumen aggregates from the bulk of the slurry to the froth layer.

With this knowledge, some suggestions have emerged to minimize the effect of the interactions between metal ions and clay to improve the bitumen recovery from poor processing ores. These suggestions include the dispersion of fine contents by diluting it below threshold value of interference with dilution water (Takamura and Wallace, 1988); blending of good processing ores with poorly processing ores to benefit from the synergy of compromising good processing ore with poor processing ores (Schramm et al., 1985); and softening water and sequestering divalent metal ions from feed water (Kotlyar et al., 1987; Schramm and Smith, 1987c; Smith and Schramm, 1992).

4.5 Discussion

We have established the laboratory procedure to study the role of metal ions, clays, and operating conditions on bitumen recovery, flotation kinetics and froth quality, and to predict the performance of a commercial unit. Using this procedure, a large variety of ores were tested and we have demonstrated that the primary bitumen recovery was more sensitive marker in reflecting responses to changes of operating variables. Our study showed that it diverts only marginally from the baseline primary bitumen recovery when dissolved metal ions (calcium, magnesium or sodium) and clays (montmorillonite, kaolinite or illite) do not interact in a synergistic manner. When dissolved divalent cations (Ca^{++} or Mg^{++}) at 1 mM concentration interact with montmorillonite clay at 1% weight of oil sands, bitumen recovery decreases by up to 26%. This decrease depends largely on the valence of dissolved cations and their concentrations, but to a less extend on the type of cations. It depends also on the type and the concentration of clays, depending of the surface area and the cation exchange capacity. The effects are found in the following sequence of importance (Bolt, 1976):

kaolinite < illite < montmorillonite

This finding suggests that, with good processing ores, a minimal synergetic effect of calcium ions in water with kaolinite, the most abundant clay mineral or with illite clays should have only a marginal negative impact on bitumen flotation, as compared with the presence of montmorillonite clay. Due to its greater surface area and ion exchange capacity, montmorillonite clay, the less abundant clay in ore, forms a barrier of slime coating on bitumen. A layer of hydrophilic clay particles formed as such masks the hydrophobic bitumen surfaces, preventing bitumen attachment to air bubbles. The uptake of calcium by montmorillonite clay from water was determined to be about 4.6 mg calcium per gram of clay. Bitumen recovery was depressed in doping tests by fines that were recycled from poor processing ores or by 15% kaolinite clay added to a good processing ore. A depression of 32% bitumen recovery was observed when 13% kaolinite clay and 40 ppm calcium ions were mixed with the good processing ore, confirming the detrimental effects of diluting ore grades and of the interactions between clays and metal ions on processability. Depression of bitumen by clays addition is marginal with sodium in water up to 1000 ppm. Our results suggest that the ionic strength due to addition cations to the slurries cannot be used alone to explain the observed variation of bitumen recovery.

The addition of caustic as a process aid allowed maintenaning good bitumen recoveries by partially alleviating the negative impact of calcium ions interacting with fine montmorillonite clays on bitumen flotation. The slime coating was found to be less severe at high pH with caustic addition. For the low grade ore sample tested in this study, caustic addition at 0.01% improved bitumen recovery only marginally by 3%; at 0.04%, it depresses even more bitumen recovery. This finding suggests that poor processing ore behaves differently to the caustic addition; its optimal addition must be narrowed for each poor ore type although bitumen recovery may be improved also with longer retention time of flotation.

When sodium bicarbonate ($NaHCO_3$) is added prior to conditioning as a process aid, it precipitates calcium from water and hence minimizes bitumen recovery depression. In fact, a slightly better bitumen recovery than the baseline results was obtained in this case. However, when it is added after bitumen is depressed; the improvement of bitumen recovery by sodium bicarbonate addition is very marginal. In this case, sodium bicarbonate addition does not restore bitumen recovery. It can be concluded that precipitating metal ions would mitigate their detrimental effect on bitumen recovery. However, when clay is attached to bitumen, this slime coating is so strong that it resists the effect of bicarbonate in restoring bitumen hydrophobicity. We have found also that in spite of the common perception that high grade ores have higher recoveries than poorer grade ores; some higher grade ores (12.8-13.6 % bitumen) showed lower primary recovery and slower bitumen recovery kinetics than the lower grade ores (10.3-10.74 % bitumen).

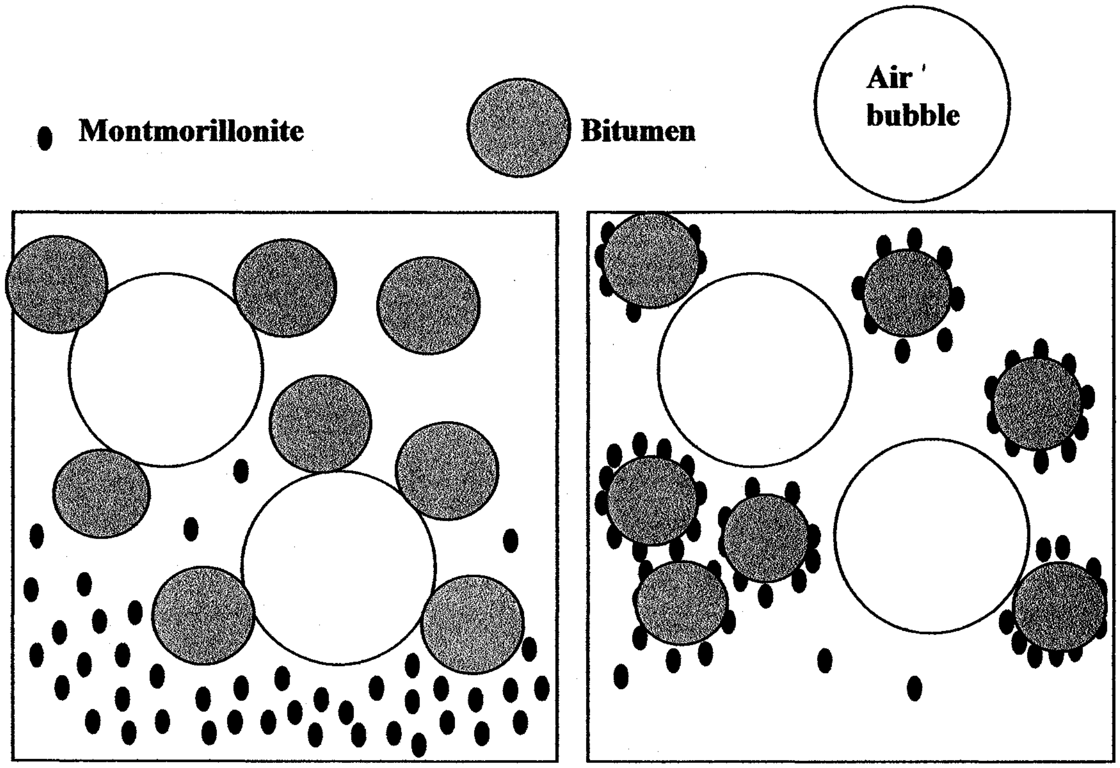
Bitumen recovery was found to be insensitive to temperature variations above 50°C. Bitumen flotation kinetics is drastically affected by the decrease of temperature from 50°C to 25°C for some ores tested. Flotation at 50°C was found to be sufficient to reach maximum bitumen recovery; but care must be taken to consider the froth quality. At a temperature lower than 50°C, longer conditioning times are recommended. The Low Energy Extraction processes are viable below 50°C with the use of lengthy conditioning pipelines to compensate for the decrease in temperature. For poor processing ores, the following solutions would help to improve bitumen recovery.

Ore blending would help to dilute the fines content. Water softening would help by sequestering of calcium and magnesium ions into less reactive precipitates and hence reducing their content in water and preventing depression of bitumen recovery.

Future work requires developing a further understanding of the effect of flocculent as a process aid for poor processing ores with the intention of minimizing hetero-coagulation of bitumen with fines. This approach would also be beneficial by adding value to tailings management.

4.6 Claims

1. The main contribution of this research to the original knowledge of depression mechanisms of bitumen recovery from poorly processing ores is the development of a novel approach of doping a good processing oil sands ore with a controlled amount of calcium/ magnesium and clays addition. It helps studying the role of water chemistry and ore characteristics in bitumen flotation.
2. The miniaturization of the visualization technique allows us also to identify the loss of bitumen hydrophobicity, quantified by the contact angle measurement, as the cause for depression of bitumen recovery.
3. Our results from doping tests and the visualization technique clearly show that understanding the interactions of metal ions and clays would help in evaluating their role in bitumen recovery from oil sands ores.
4. The disappearance of calcium and magnesium ions from the process water was observed when montmorillonite clay was added, but not when kaolinite or illite clays were added.
5. The metal ions adsorbed on montmorillonite clay would interact with carboxylic groups of natural surfactants on bitumen droplets, resulting in slime coatings of bitumen by montmorillonite clay, that is schematically shown in the in Figure 4-33, that makes bitumen surface to be less hydrophobic resulting in poor floatability.
6. This suggests that the depression of bitumen recovery was associated with a strong affinity between metal ions and montmorillonite clay that has larger specific surface area, stronger cation exchange capacity and higher adsorption capacity for metal ions compared with kaolinite or illite clay characteristics.



<u>No slime coating,</u>

- strong air-bitumen attachment
- high recovery
- high froth quality

<u>With slime coating,</u>

- poor air-bitumen attachment
- low recovery
- low froth quality

Figure 4-33: Concept of the effect of slime coating on bitumen surface during flotation

7. In this research work, we have found that bitumen recovery correlated well with changes in the receding water contact angle.
8. We have shown that measured zeta potentials of three different clays were all negative in the pH range encountered in industrial oil sands processing. The addition of divalent calcium cations at 1 mM/L was not sufficient to cause surface charge reversal for clays.
9. The measured zeta potential of clays and the surface tension of the supernatants from the flotation slurry did not correlate with bitumen recovery.
10. Our findings illustrate that for our operating conditions, the key factors that depress bitumen recovery are the type and concentration of clays/fines coupled with the concentration and the valence of cations but the type of metal (Ca^{2+}, Mg^{2+}) plays a secondary role in depressing bitumen recovery.
11. The practical implication of our results is that the adverse effect of increasing calcium ion concentration in process water would not be observed for oil sands ores of low fine contents, such as estuarine ores. A depression of bitumen recovery is anticipated for ores containing a substantial amount of smectite fine clays, such as weathered illite and/or montmorillonite clays.
12. The findings from our doping tests are summarized in Figure 4-34 that shows that bitumen recovery is depressed by the addition of 1% montmorillonite with calcium ions over 40 ppm or strongly by magnesium ions over 24 ppm, but not by calcium in precipitated form nor by sodium ions below 1000 ppm. Sodium hydroxide was found to be effective at restoring bitumen recovery while sodium bicarbonate did not.

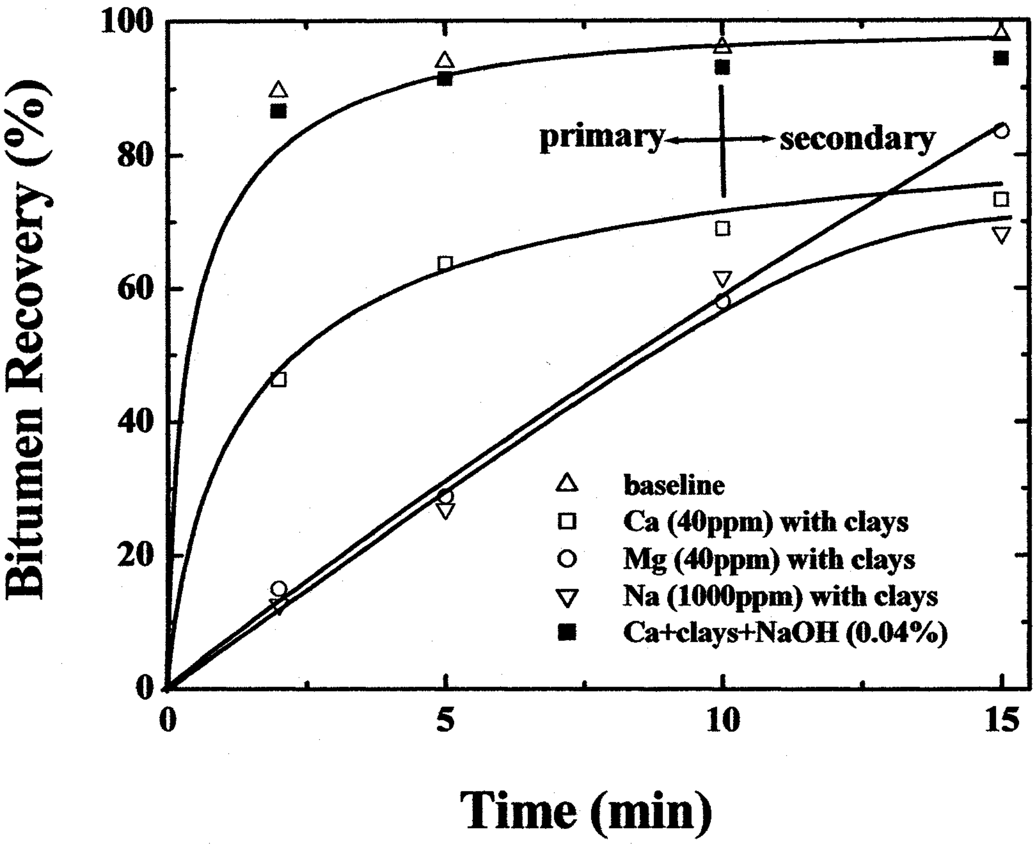


Figure 4-34: Effect of metal ions (calcium and magnesium at 40 ppm and sodium at 1000 ppm) in deionized water at 76°C in the presence of 1% montmorillonite clay doped to good processing ore samples in depressing bitumen recovery and effect of caustic addition (0.04%) in restoring depressed bitumen recovery

CHAPTER 5

MECHANISTIC STUDY

In this chapter, we study bitumen depression mechanisms by examining dependent variables. The focus is on the importance of water chemistry and clays as sources of bitumen recovery depression. We will consider how the correlations fit with observed processability for various types of ores tested. To explain the insights of the mechanisms of depression of bitumen recovery derived from our novel doping test and visualization technique, the extraction systems were characterized by cation adsorption, surface tension, contact angle, induction time, zeta potential and colloidal forces measured using atomic and surface force microscopy.

5.1 Adsorption of Metal Ions from Solutions

The process tailings water from doping tests was centrifuged and recovered for analyses. We used the atomic absorption spectrophotometer to determine the residual calcium ion concentration as result of water softening due to its adsorption on bitumen and clay surfaces. Results are summarized in Table 5-1 and show that in the absence of calcium ion and clays additions, the concentration of calcium ions released by the high grade oil sands ore sample was only 0.5 ppm. This measurement is within the accuracy of the detection limit of the atomic absorption analytical method for such water quality containing number of detectable elements (Ewing, 1960). This corresponds to the baseline condition that is characterized by high bitumen recovery. In contrast, the Figure

4-15 shows that a level of 12 ppm calcium ions was detected in the tailings water samples from a low grade oil sands slurry sample known for its low bitumen recovery.

Table 5-1: Measured residual calcium concentration in process tailing water

Ore types	**Clays addition**	**Ca^{2+} addition (ppm)**	
		0	40
		Residual Ca^{2+} (ppm)	
Good processing ore	None	0.5	27.4
Poor processing ore	None	12	-
Good processing ore	1% Illite	0.5	21.4
Good processing ore	1% Kaolinite	0.3	21.0
Good processing ore	1% Montmorillonite	0.1	3.0

In the absence of calcium addition, the addition of clays alone to the high grade oil sands ore slurry did not change the residual calcium ion concentration (0.1 to 0.5 ppm), suggesting that no additional calcium ions were released from the added clays.

In the absence of clays, the addition of 40 ppm calcium ions alone to the high grade oil sands slurry resulted in a residual calcium ion concentration of 27.4 ppm in the process tailings water. This shows 32% reduction of calcium ions in tailings water, suggesting that an uptake of 12.6 ppm calcium ions or 0.027 mg calcium per gram of oil sands ore would cause only a marginal decrease in primary bitumen recovery as seen in Figure 4-5. In the presence of 40 ppm calcium ions and 1 wt% kaolinite or illite clays additions to the high grade oil sands slurry, about 21 ppm calcium ions remained in the tailings water. Since we have established that the addition of clays did not release additional calcium ions into the slurry, this further reduction of 6.4 ppm calcium ions accounts for 1.2 mg calcium uptake per gram of clays. This depression of bitumen recovery is still marginal in spite of increase in the uptake of calcium to 48%.

However, in the presence of 40 ppm calcium ions co-added with 1 wt% montmorillonite clay, further reduction of 24.4 ppm calcium ions from 27.4 ppm to 3 ppm was observed. This accounts for 4.6 mg calcium uptake per gram of montmorillonite clay. Calcium up taken was increased to 92% and this caused about 26% depression of bitumen recovery. The results summarized in Figure 5-1 collectively suggest a minimal synergetic effect of calcium with illite or kaolinite, but a noticeable synergetic effect of calcium with montmorillonite on bitumen recovery.

5.2 Surface Tension of Process Tailings Water

Measurements of surface tensions of process tailings water are shown in Table 5-2, they range between 57.9 and 59.9 mN/m that is significantly lower than the surface tension of deionized water (71.7 mN/m). The reduction in surface tension is a convincing indication of surfactant release to process water. Bowman (1967), Moschopedis et al. (1977), Ali (1978), Sanford and Seyer (1979), Schlamm and Smith (1987) and Schramm et al. (1984)

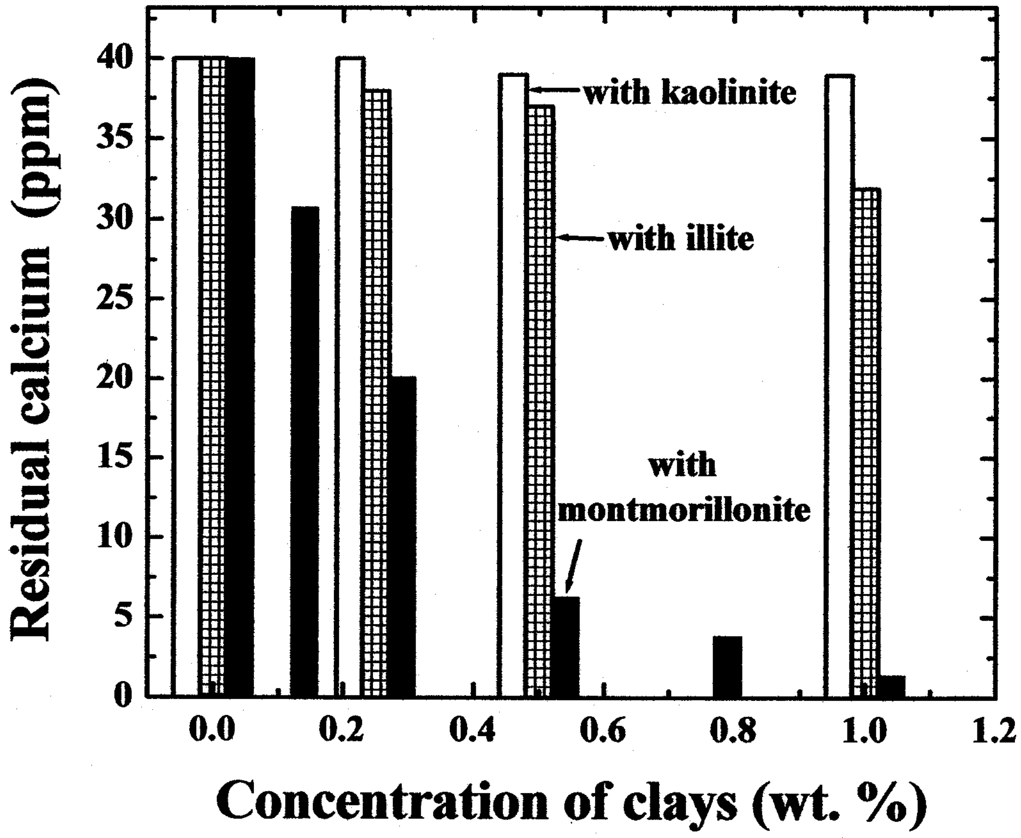


Figure 5-1: Residual calcium ions concentration in process water after uptake by different types and concentrations of clays in deionized water containing 40 ppm Ca^{2+}

reported the release of certain amount of free surface active species from bitumen into the water during conditioning of oil sand ore. They were identified as carboxylate ($RCOO^-$) and sulphonate (RSO_3^-) types of surfactants.

Table 5-2: Measured water surface tension

Water types	**Ca^{2+} addition**	
	0 ppm	40 ppm
	Water surface tension (mN/m)	**Water surface tension (mN/m)**
Deionized water alone (DI)	71.7	70.6
Oil sand tails water (OTW)	58.6	57.2
OTW with 1% Montmorillonite	57.9	59.9
OTW with 1% Illite	57.9	59.2
OTW with 1% Kaolinite	57.8	59.2

Their presence decreases the surface tension (Chow and Takamura, 1985 and 1988), which is considered a fundamental requirement for detachment of bitumen from sand surfaces. Surfactants also contribute to the generation of abundant fine bubbles in process water from high fine ore slurries (Zhou, 2000).

Figure 5-2 shows a scatter in the distribution of measured surface tensions of process tailing water, it does not show any correlation between surface tension and bitumen recovery. This absence of correlation suggests that, under our experimental conditions of doping tests, bitumen recovery is not sensitive to the surface tension of process water. Clearly, the surface tension alone cannot be used as a useful marker in characterizing and assessing the role of water chemistry in bitumen recovery by flotation from oil sand ores.

5.3 Hydrophobicity and Contact Angle Measurements

Figure 5-3 summarizes changes of the attachment between air bubbles and bitumen in different environments. Figure 5-3(1) shows the syringe arrangement that makes air bubbles to attach to a bitumen surface.

Figure 5-3(2) shows typical images of good processing ore with a strong attachment. It is seen that when the micro-syringe was moved away from the bitumen surface, the air bubble remained on the bitumen surface. It was not withdrawn back into the syringe, and the air bubble-bitumen contact did not break. Instead, the air bubble itself broke, leaving part of itself on the bitumen surface as shown in Figure 5-3(2-D). This suggests a strong attachment of air bubbles to bitumen for a good processing ore, accounting for good bitumen recovery.

Figure 5-3(3) shows that for a poor processing ore, air bubbles detached totally from bitumen surfaces due to weak air-bitumen attachment. That leads to low bitumen

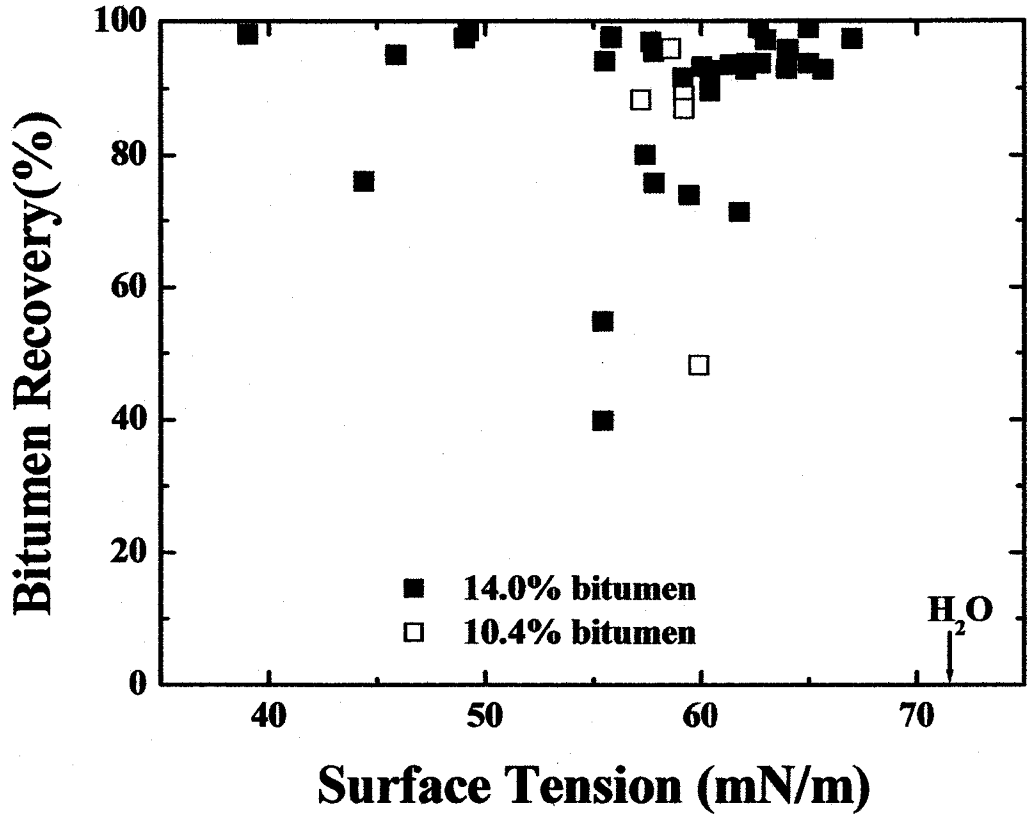
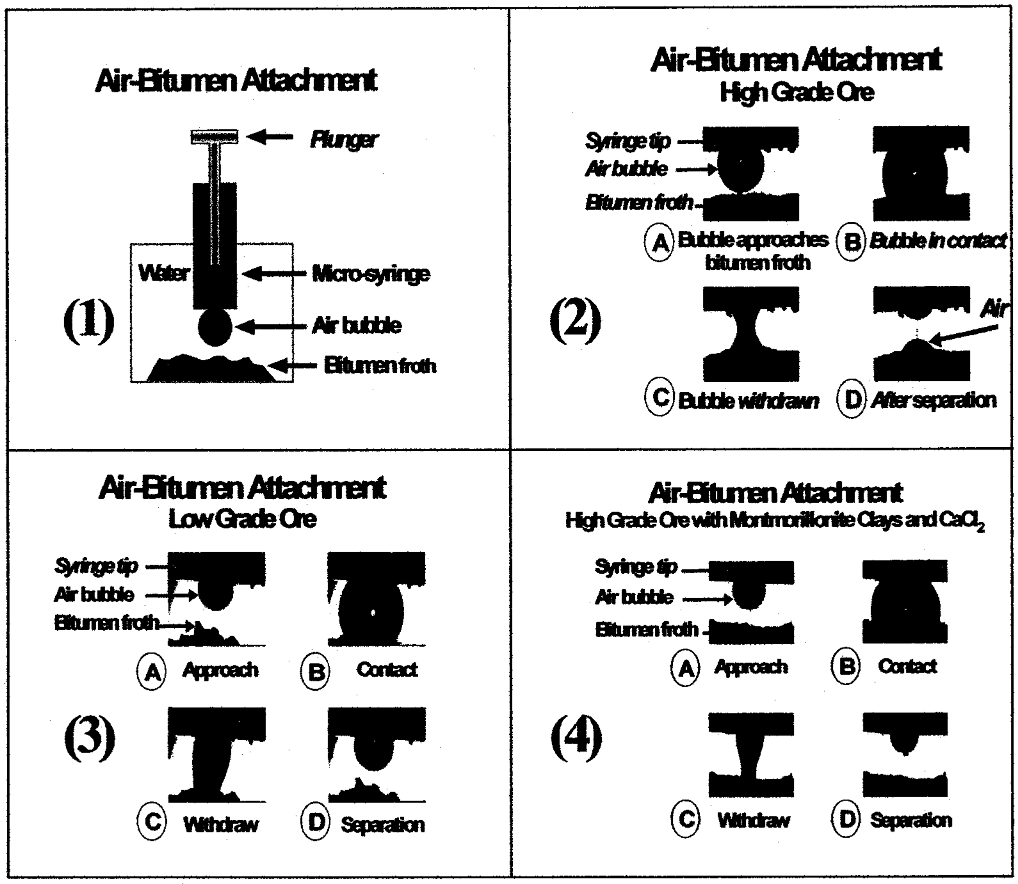


Figure 5-2: Lack of correlation between bitumen recovery and surface tension measured on process water collected from bitumen flotation



Air bitumen attachment under different environments

(1) Syringe arrangement

(2) Air-bitumen for a good processing ore

(3) Air-bitumen for a poor processing ore

(4) Air-bitumen attachment test for good processing ore with added calcium and montmorillonite clay

Figure 5-3: Air bubble-bitumen attachment after Zhou et al (2003) recovery of 70% as shown in Figure 4-20. A similar result is seen in Figure 5-3(4) for a doping test of good processing ore poisoned with 40 ppm calcium ions and 1% montmorillonite clay. Figure 5-4 shows the measurement of contact angles of bitumen in water during conditioning under doping test conditions. It shows in the upper curve that when calcium addition is increased from 0 to 40 ppm in the absence of montmorillonite clay, the contact angle of naturally hydrophobic bitumen decreased marginally from 60° to 50°. At 0 ppm calcium ion addition, a marginal reduction in contact angle from 60° to 50° (upper to lower curve) was also observed when bitumen was conditioned with 0.5 wt.% montmorillonite fine clays. A drastic change in contact angle, decreasing from 50° to less than 20°, was observed when bitumen was conditioned in 0.5 wt% montmorillonite clay suspensions with calcium ion concentration increased from 0 to 40 ppm. The reduced contact angle shown in Figure 5-4 occurs in the doping test conditions characterized with substantial uptake of calcium ions from water by montmorillonite clay. The uptake of calcium ions from water by montmorillonite clays in Figure 5-1 is due to the high surface area for this clay type. The decrease of contact angle reflects the weak attachment between bitumen and air bubble that is observed in Figure 5-3(4) as result of depression of bitumen recovery shown in Figure 4-6.

Figure 5-5 shows a general correlation between contact angle and primary bitumen recovery. It was measured in deionized water at room temperature after bitumen surfaces were conditioned in slurries of corresponding doping conditions. It shows that a larger contact angle at 60° indicates a stronger bitumen hydrophobicity resulting in a strong attachment to the air bubbles during flotation making bitumen easy to attach to air

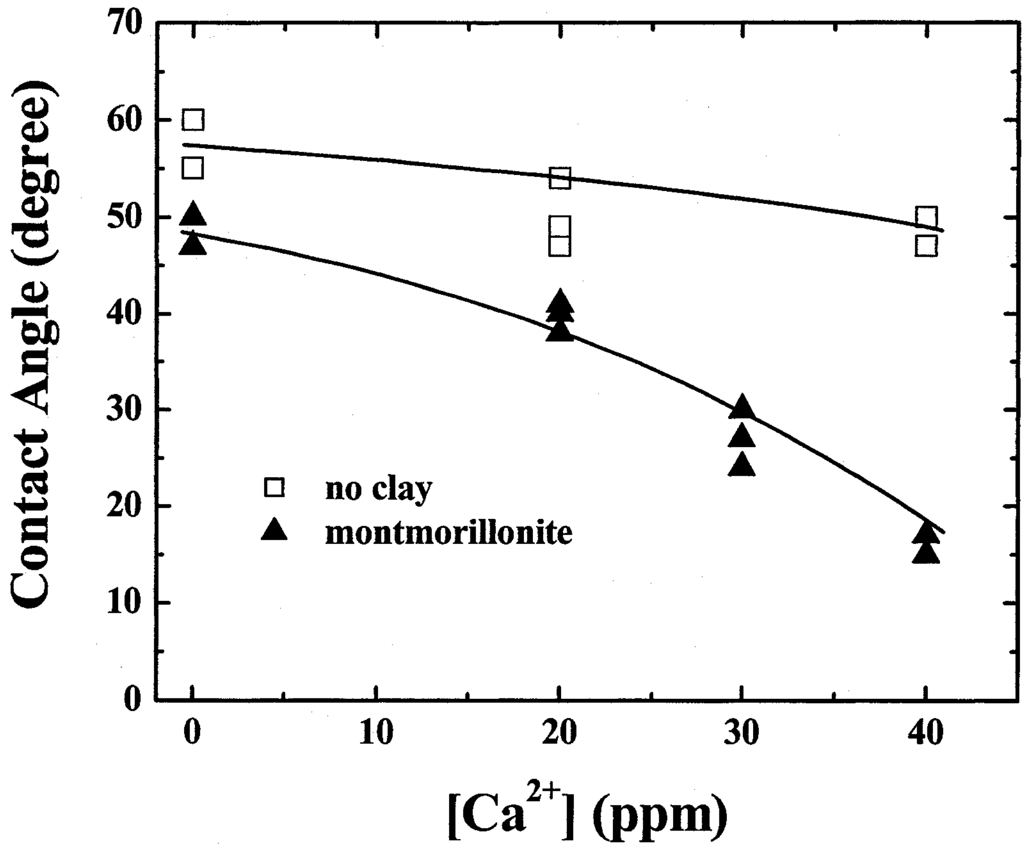


Figure 5-4: Effect of Ca^{2+} ions concentrations on contact angle in absence and in the presence of 1% montmorillonite clay using deionized water

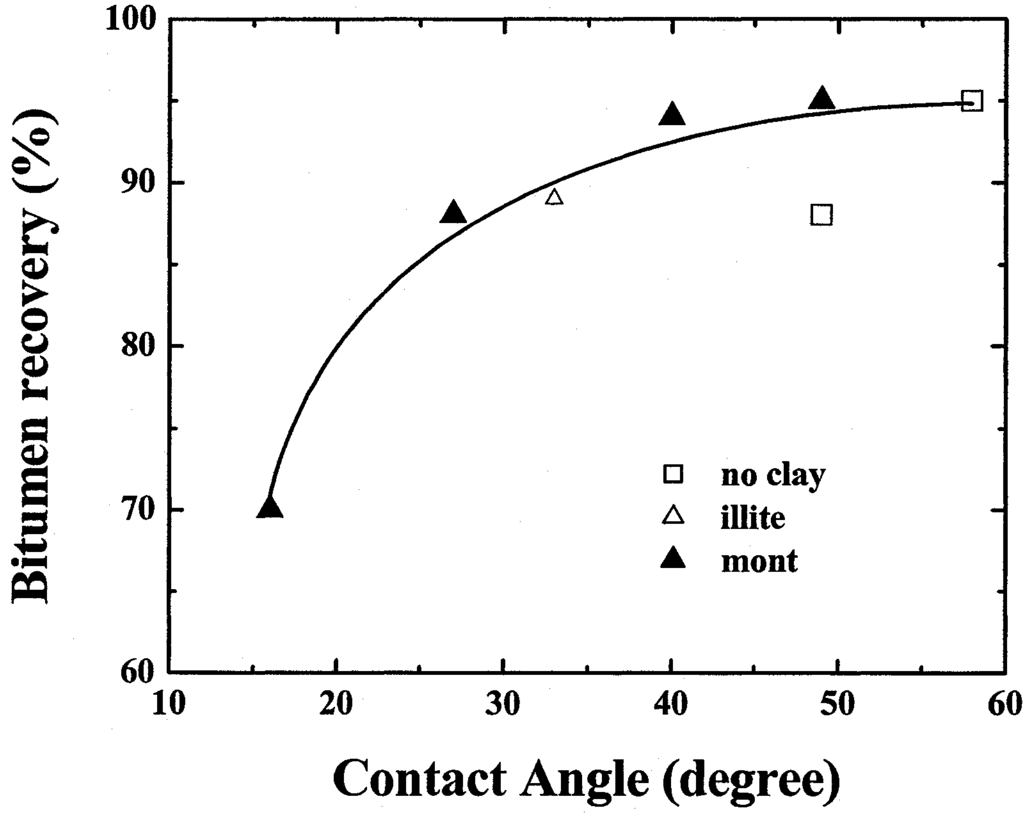


Figure 5-5: Correlation between primary bitumen recovery and contact angle

bubbles and to report to the froth zone. This accounts for the observed highest primary bitumen recovery (over 92%) for good processing oil sands ore in the absence of additives (Kasongo et al., 2000; Zhou et al, 2003a). This is evidence that the wettability is an important marker in determining bitumen flotation. It is interesting noting that such result was not observed when calcium was added with kaolinite or illite clays but only with montmorillonite clay.

5.4 Effect on the Induction Time (Gu, 2000)

The induction time was used to characterize air bubble-bitumen attachment when bitumen hydrophobicity was modified by the slime coating effect. The measurements were performed by Gu (2002, 2003) on samples collected from doping tests flotation. The induction time is defined as the time for thinning and rupture of the intervening film between an air bubble and bitumen surface and the formation of a stable air bubble-bitumen attachment. It was measured in de-ionized water, clear process water obtained after centrifugation, and process water containing 0.5% fine solids in the presence and in the absence of 50 ppm Ca^{2+} addition made at different temperatures.

Figure 5-6 shows that at 25°C, the induction time of air bubble-bitumen attachment was the shortest in de-ionized water without additives. It was the longest in the process water containing 0.5% fine solids in the presence of 50 ppm calcium ions. This increase of the induction time is due to the slime coating on bitumen by hydrophilic fine solids that act as a barrier to the attachment of air bubbles. The increase in induction time results in a decreased bitumen recovery or loss of oil into the tailings. The addition of calcium ions alone to de-ionized water or to the centrifuged process water had only a marginal effect on the induction time. The addition of fine solids alone to the clear process water showed a negligible effect on the induction time. It was demonstrated that the induction time of air bubble-bitumen attachment in all solutions decreased with increasing temperature, suggesting that higher temperatures are favorable for air bubble-bitumen attachment as shown in Figure 4-32(A) for bitumen recovered at 76°C. It is important to understand how the induction time depends on the size of air bubbles, the distance between the air bubble and the bitumen surface, the amplitude, and the impulse of the air bubble used to approach the bitumen surface.

5.5 Surface Charge and Zeta Potential Measurements

The electrokinetic properties of bitumen and clays were studied to explain the slime coating of montmorillonite clays on bitumen surfaces. Surface charges of clays were measured by electrophoresis in aqueous solutions over a pH range of 3 to 12. Figure 5-7 shows zeta potentials of each single clay suspension (montmorillonite, kaolinite, and illite), measured in the absence of calcium ions. It shows that all the clays carry negative surface charges with measured zeta potential being between –50 mV and –75 mV in the operating pH range of 7-8. In the presence of 40 ppm calcium ions, the absolute values of zeta potential decreased, but they remain negative (between –20 mV and –40 mV) as shown in Figure 5-8.

Zeta potential distributions are a powerful tool used by Liu and Xu (2002) to further comprehend findings from my work and to study the role of calcium ions in activating

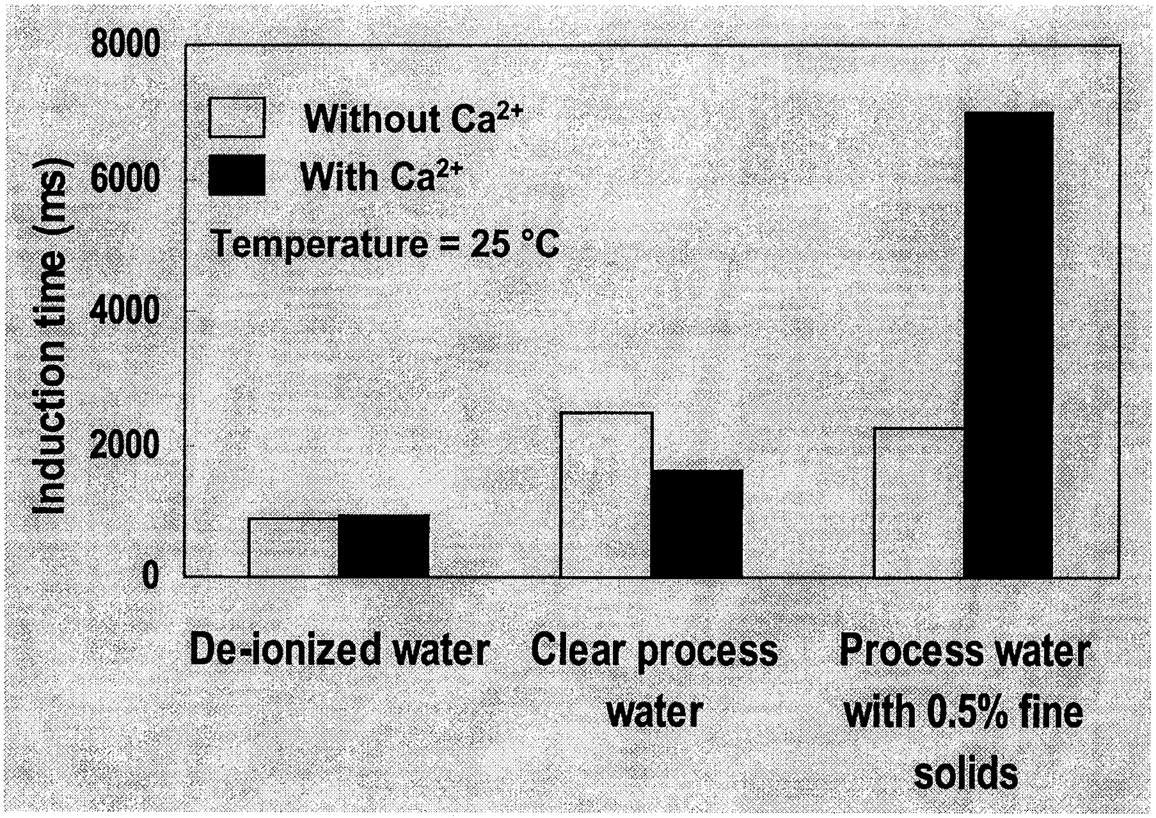


Figure 5-6: Induction time measured for pure bitumen using different water types in the absence and in the presence of 40ppm calcium doped with and without fine solids content at 0.5% water

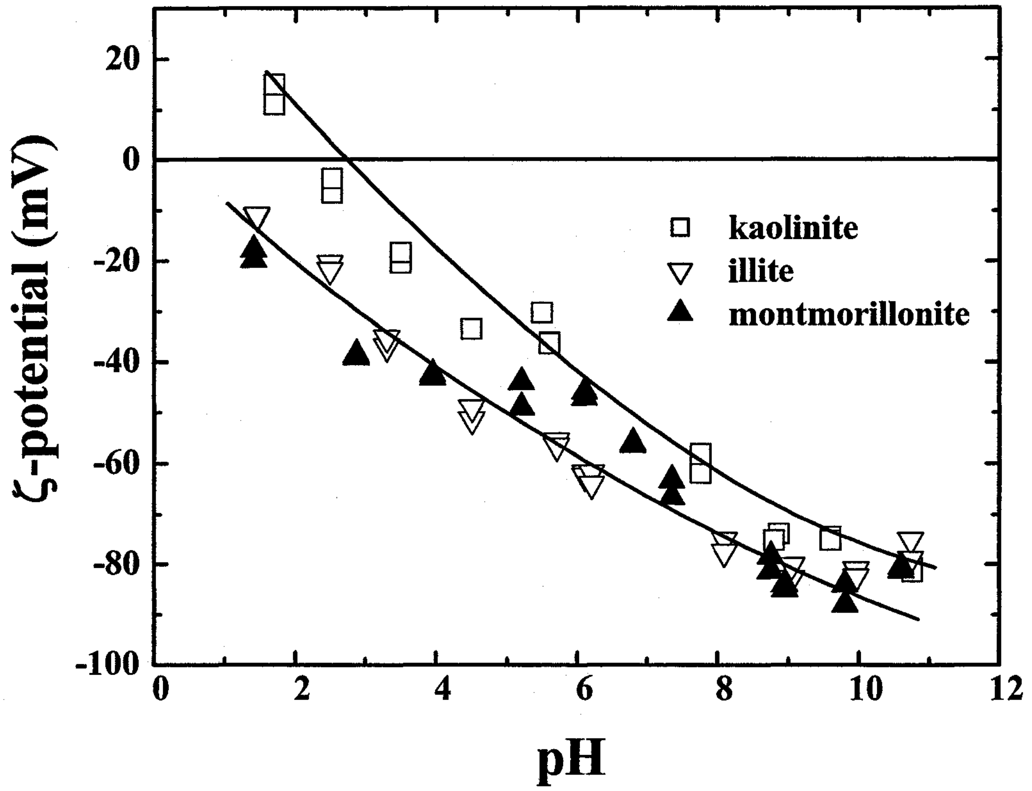


Figure 5-7: Zeta potential of clays as function of pH without calcium ions addition in water with KCl as supportive electrolyte

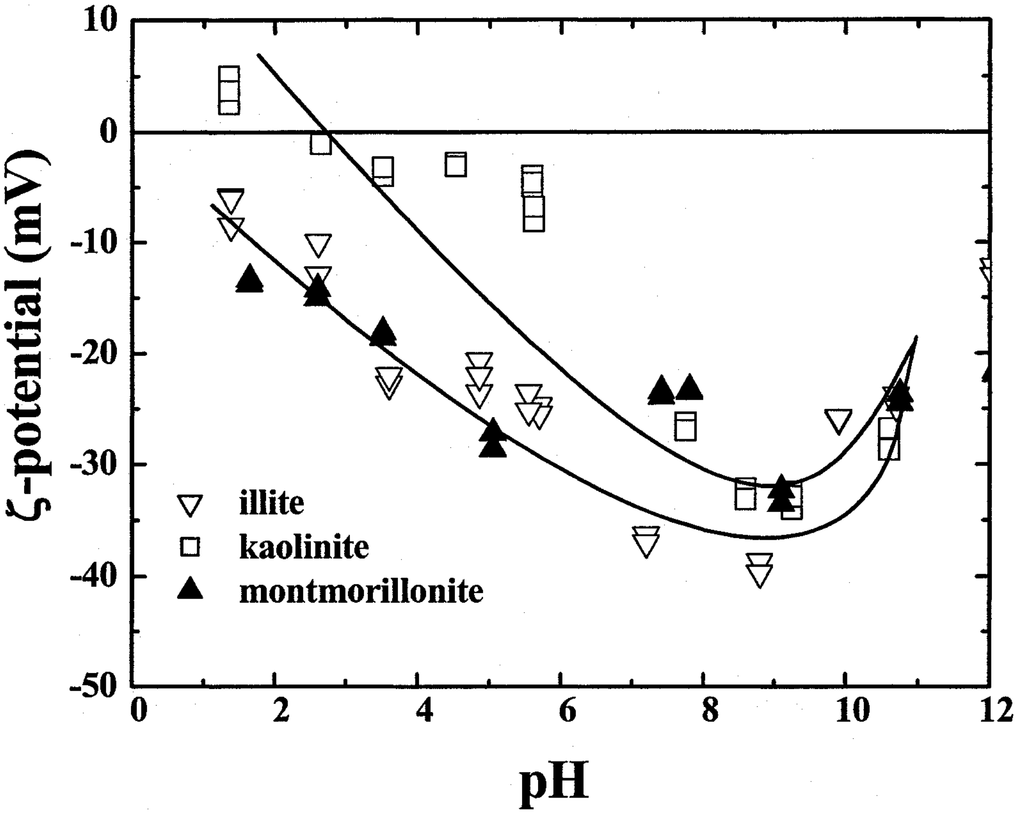


Figure 5-8: Zeta potential of clays as a function of pH with calcium ions addition in deionized water with KCl as supportive electrolyte.

slime coating of montmorillonite clay particles on the surface of bitumen droplets. Their study is summarized in Appendix 5 where measurements of zeta potential help to identify slime coating in binary suspension systems. They showed also that the zeta potential of bitumen is also negative, ranging between –60 mV and –80 mV in the operating range of pH.

This suggests that the electrostatic repulsion force would be expected between negatively charged montmorillonite clay particles and negatively charged bitumen surfaces, making the attraction impossible but a repulsion force. These observations show that in the absence of calcium ions, zeta potential change or the electrostatic interactions model alone cannot explain the slime coating of bitumen by fine montmorillonite clay, which results in the depression of bitumen recovery.

Figure 5-9 (a) shows individual distributions of zeta potentials in case of binary bitumen-clay and (b) shows their mixture without calcium ion addition. This feature suggests the absence of attraction forces between two components. It predicts a weak coagulation between bitumen droplets and clay particles that results in partial coating of montmorillonite clay particles on the surface of bitumen droplets. In contrast, Figure 5-9 (c, d and e) shows the shifting of these distributions in presence of calcium ion addition. Figures 5-9 (c) shows only one peak in the position of the clay suspension, suggesting that clay completely coated the bitumen. This is an indication of a strong attraction for bitumen droplets that are covered with montmorillonite clay particles in the mixture. Figure 5-9 (d and e) shows possible locations of peaks indicating weak attraction between

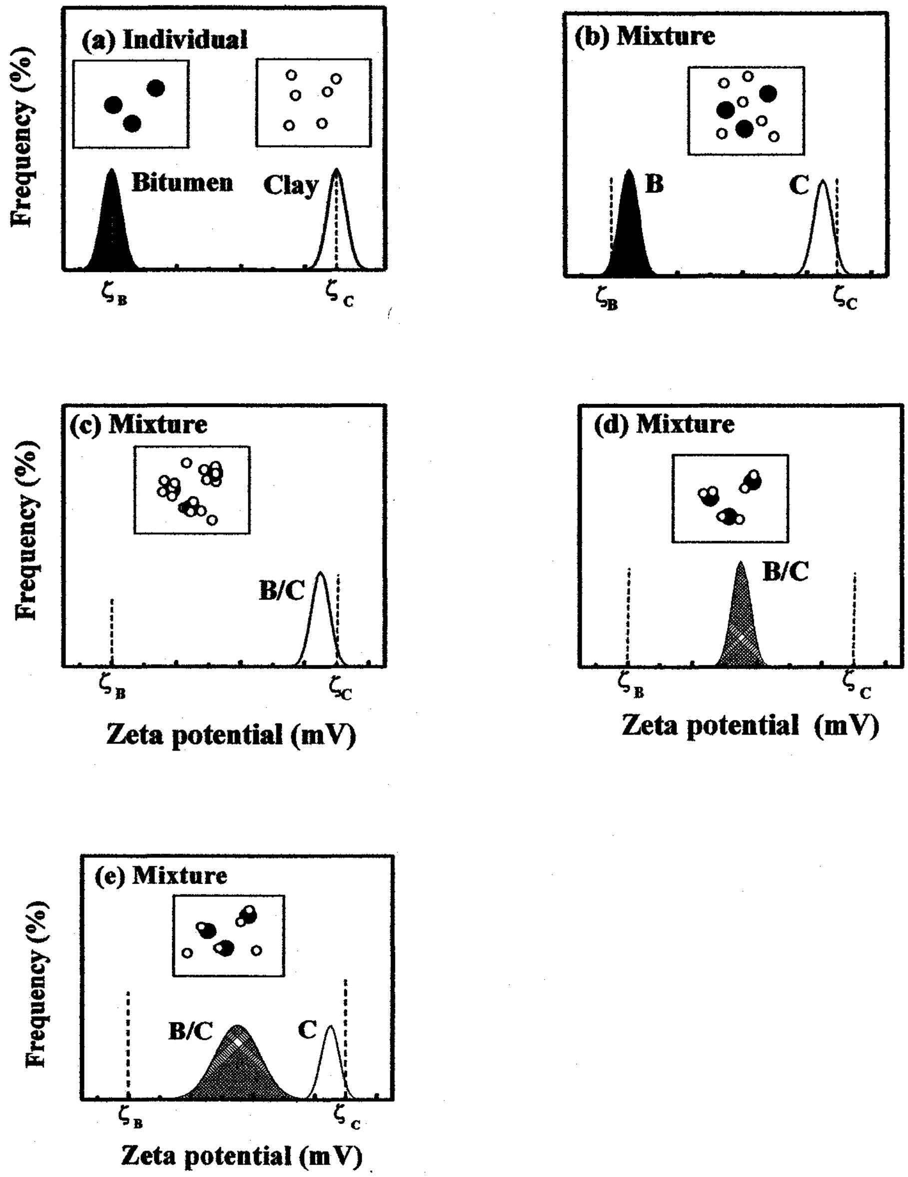


Figure 5-9: Schematic zeta potential distributions for a binary particulate component system, after Liu (2002)

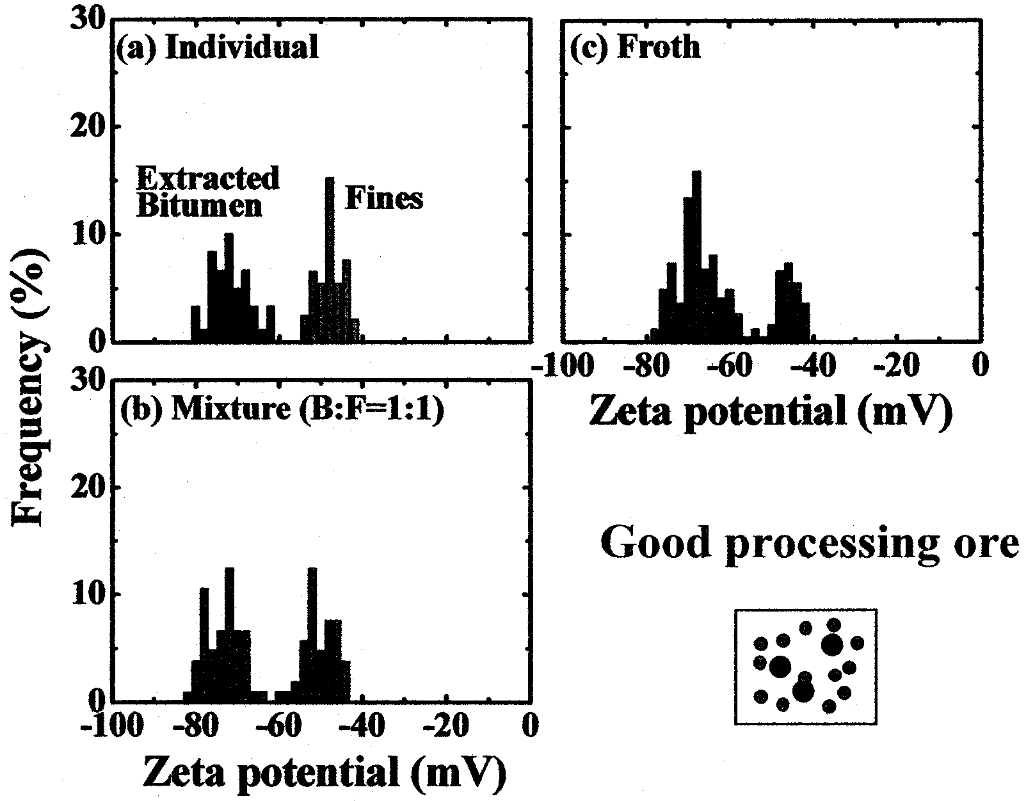


Figure 5-10: Good processing ore: zeta potential distributions for solvent extracted bitumen and fines: (a) individually, (b) mixture, (c) emulsified froth after Liu (2002) (Figure 5-14 in page 214)

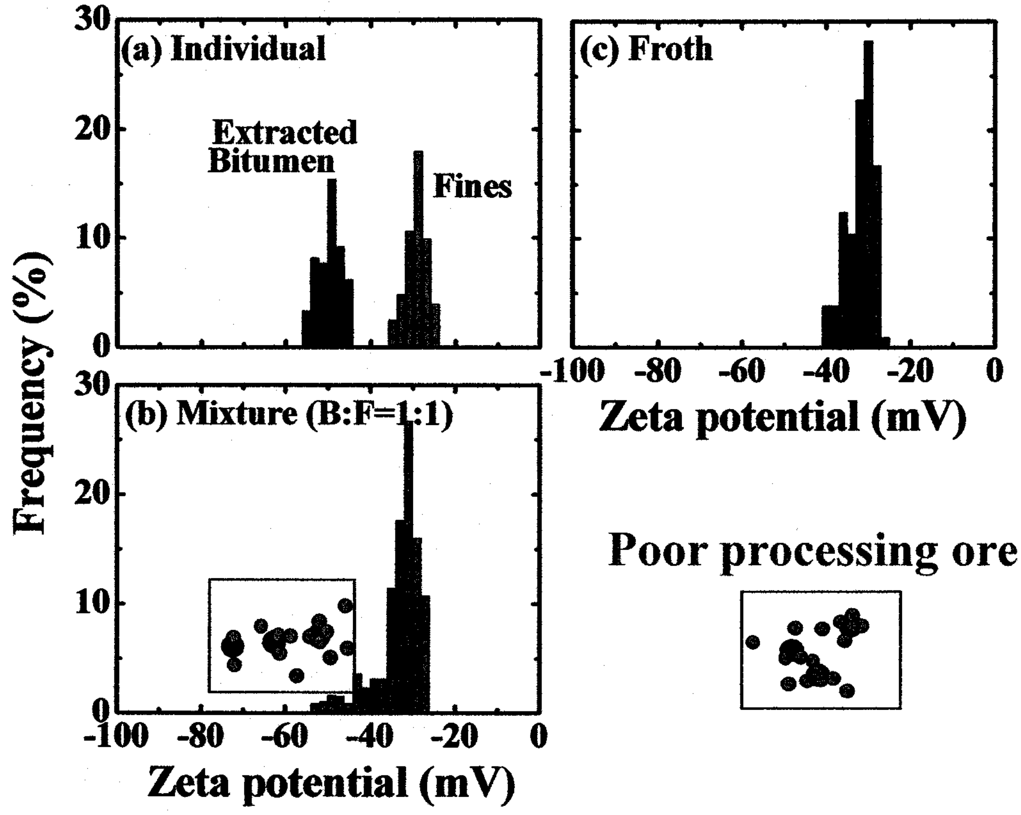


Figure 5-11: Poor processing ore: zeta potential distributions for solvent extracted bitumen and fines: (a) individually, (b) mixture, (c) emulsified froth after Liu (2002) (Figure 5-15 in page 216)

bitumen droplets and clay particles that partially cover bitumen surface where a substantial amount of individual clay particles remain unattached to bitumen. The findings confirm a weak interaction shown in Figures 5-10 (5-14 in page 214) and the absence of coagulation and slime coating of fines on bitumen for good processing ore preserving the hydrophobicity of bitumen. In contrast for poor processing ores in Figures 5-11 (5-15 in page 216), strong coagulation of fines with the surface of bitumen, forming a slime coating that changes the bitumen surface to become less hydrophobic and resulting in weaker air bubble-bitumen attachment and poor bitumen recovery.

5.6 Atomic Force Microscopy Measurements (Lui et al., 2002)

The slime coating effect was also studied by measuring the distribution of the adhesion force between montmorillonite clay and bitumen with and without calcium ions. Figure 5-12 shows that without calcium ions at pH 8.2, the adhesion force was centered at 4 mN/m. But with 1 mM calcium, it is stronger and centered at 9 mN/m due to the bridging effect of calcium ions between bitumen and clay particles. This produces a bitumen surface that is coated with fines, decreasing its hydrophobicity and attachment to air bubbles and hence leading to a decrease in bitumen recovery.

5.7 Conclusions

5.7.1 General findings

1. The doping test, the visualization technique and further fundamental studies were initiated to help contribute to better understand the depression of bitumen recovery during flotation for poisoned good processing ores.

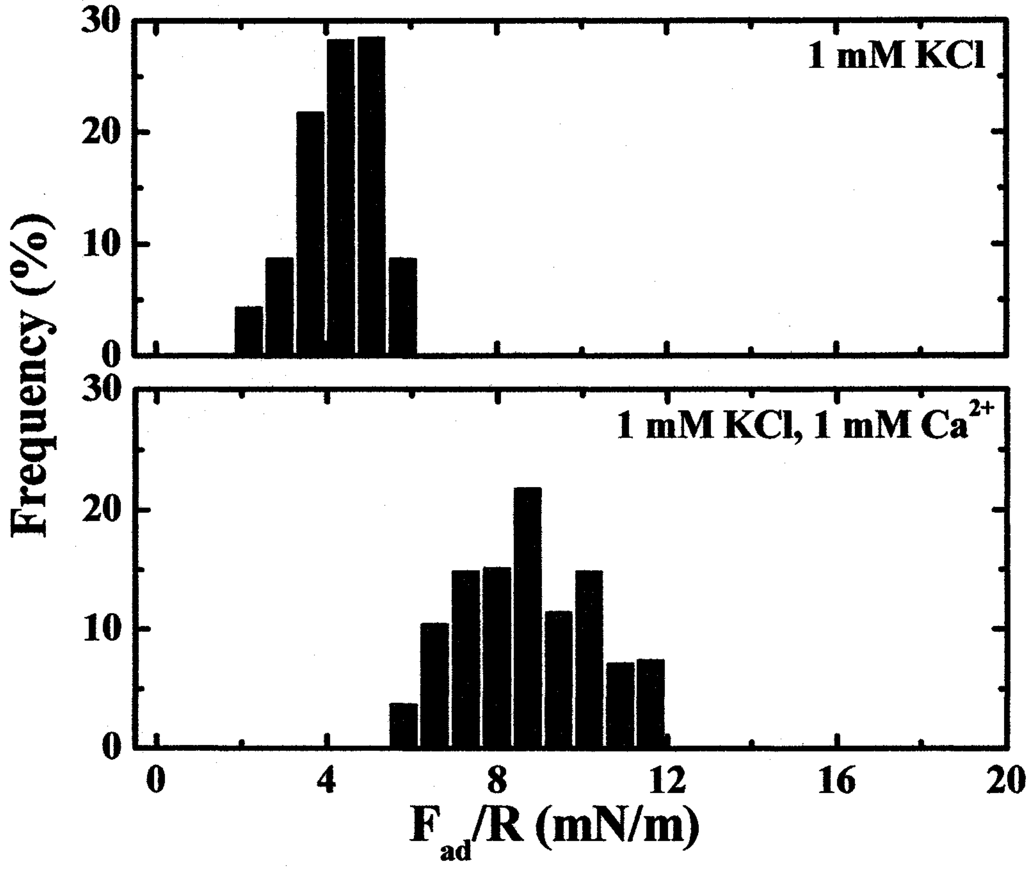


Figure 5-12: Effect of calcium addition on normalized adhesive forces between bitumen and montmorillonite clay in 1 mM KCl solution: (a) without calcium; (b) with 1 mM calcium after Liu (2003)

2. This gave access to an insight to the mechanisms of depression of bitumen recovery. from poor processing ores.
3. The fundamental study of the effect of co-addition of fine clays and divalent ions on depression of bitumen-recovery during extraction process was based on experimental measurements and observations as: the uptake of calcium ions from water in presence of montmorillonite clay, the correlation between contact angle and bitumen recovery, the use of zeta potential to identify the slime coating of bitumen by fine clays, the induction time and the measurement of force between bitumen and fines in water.
4. A phenomenological model, shown in Figure 5-13, suggests that the coating of bitumen surfaces by hydrophilic montmorillonite clays results from the binding effect provided by calcium ions acting as bridge (Gu, 2000; Masliyah, 2001).
5. Research work has validated the model and significant progress has been made in understanding water-based bitumen extraction from Athabasca Oil Sands.
6. However there is still no satisfactory explanation as to why, in the presence of calcium ions, slime coating was observed with montmorillonite clay but not with kaolinite or illite clays in the operating range of pH (7.5-8.5).
7. In spite of progress made, understanding mechanisms of depression of bitumen recovery from poor processing ores is still a challenge as outlined in a recent review by Masliyah et al (2004).

5.7.2 Claims from research

The general claims that allow to suggest that the major mechanisms responsible for the decrease of bitumen recovery are those that decrease bitumen hydrophobicity:

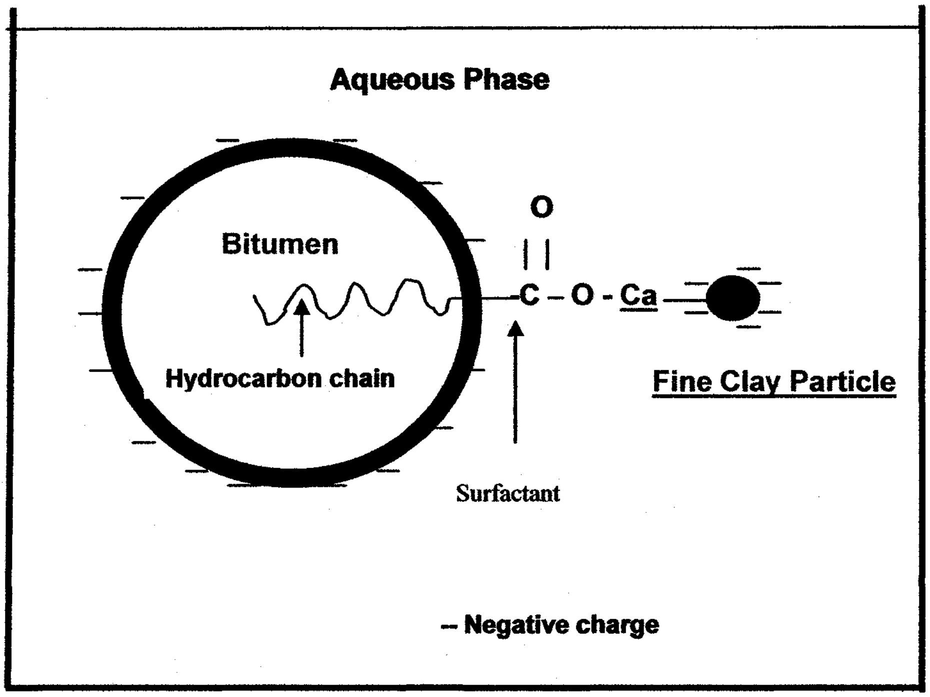


Figure 5-13: Model of interaction between bitumen, calcium and a fine clay particle

1. Bitumen surface is hydrophobic and it is negatively charged due to the presence of carboxylic groups. Montmorillonite clays surface is hydrophilic, it is also negatively charged. In this respect clay should repulse from bitumen surface.
2. In the presence of divalent ions (Ca^{2+}, Mg^{2+}) addition from doping tests, negatively charged montmorillonite clay surface attaches to the negatively charged bitumen surface. The doping test simulates plant processing operation where fines are recycled with the dilution water and metal ions with river or reclaimed water from tailings.
3. These positively charged ions tend to act as a bridge by interacting with the surfactants on the negatively charged bitumen surface and with the negatively charged surface of montmorillonite fine clay solids. This formed a slime coating that is hydrophilic that hides the hydrophobic surfaces of bitumen, reducing its attachment with air bubbles.
4. The measured contact angle of bitumen will decrease. Falling below a critical receding contact angle value (around 30^o) will results in good processing ore behaving like a poorly processing ore showing severe depression of bitumen recovery during flotation.
5. The disappearance of calcium from feed water in presence of good processing ore could be a useful indicator for diagnosing depression conditions of bitumen recovery. However, poor processing ore would release its calcium ions in water from saturated smectite fine clays that are responsible for the poor processability of associated ores.

CHAPTER 6

CONCLUSIONS, CLAIMS FROM THIS RESEARCH WORK AND SUGGESTIONS FOR FUTURE WORK

This chapter summarizes our research work, major findings and contributions to the understanding of depression mechanisms of bitumen recovery during the hot water extraction process. It also suggests a path forward for future work to shed more light on the depression of bitumen recovery from poor processing ores.

6.1 Contribution to the original knowledge

Our contribution to the original knowledge is based on the innovative doping test and on the development of the visualization technique. They were applied on real oil sands ore samples using a laboratory Denver flotation cell to study the mechanisms of depression of bitumen recovery from poor processing ores. The doping test consists in poisoning good processing oil sands ores with additives such as calcium or magnesium ions and clays to simulate poor processability by making them to behave like poor processing ores that are not sensitive to the variation of additives. The imaging technique allowed visualizing the aggregates air bubbles-bitumen that rises to the froth zone. It has helped to interpret changes in the hydrophobicity of bitumen surfaces by showing strong attachment with bitumen engulfing air bubbles when bitumen recovery is favored or weak attachment with poorly loaded air bubbles when bitumen recovery is depressed by doping good processing ores with additives.

1) Understanding the interaction between metal ions and clays has helped to evaluate their role in depressing bitumen recovery during flotation. Findings from this research work have inspired and helped to initiate many further studies aimed at understanding the depression mechanisms of bitumen recovery when poor processing ores are processed.
2) We have linked diverse theories to the depression of bitumen recoveries to explain the mechanisms and evaluate possibility of correlations with bitumen recoveries. Contact angle measurements were used to measure changes in surface hydrophobicity, surface tension to evaluate the effect of surfactants, zeta potentials to characterize the slime coating effect, adsorption to evaluate the uptake of metal ions from water, atomic force microscopy (AFM) and induction time to measure the force of a steric barrier due to the hydrophilic slime coating on the bitumen surface.
3) We have found that the effect of metal ions depends mainly on the valence and concentrations of cations, but not on the type of cations. Also the ionic strength of the slurries could not alone explain the observed depression of bitumen recovery.
4) We have shown also that the depression of bitumen recovery depends on the type of clay showing that montmorillonite clay interacts with metal ions to depress bitumen recovery but not kaolinite and illite clays.
5) The doping tests has shown that dilution of ore grades with high fines or high kaolinite addition as recycled in commercial operations in the presence of calcium ions would cause depression of bitumen recovery because of changing ore characteristics from good processing high grade ore into poor processing low grade ore.

6) We have found that for good processing ores some very high grade ores showed slower bitumen recovery kinetics compared to lower high grade ores.

7) Our findings suggest that ore blending would minimize the negative effect of reactive clay, will help to avoid dilution of oil sand bitumen grade and will help synergy of good processing ores in the blend to mitigate the depression of bitumen recovery.

8) Our work suggests also softening of high calcium water to precipitate metal ions. Caustic addition at 0.04 wt % allowed restoring bitumen recovery from good processing ores doped with calcium ions and montmorillonite clay. However applied to real low grade ore samples tested at 0.01wt %, caustic addition improved bitumen recovery very marginally and it depressed bitumen recovery at 0.04 wt % additions. Sodium bicarbonate ($NaHCO_3$) acted as scavenger of metal ions by precipitating calcium out of water, mitigating depression of bitumen recovery and improving processability when added to water prior to conditioning. But it failed to restore bitumen recovery and to overcome the strength of attachment of slime coating from bitumen surface after it is already fully depressed.

9) We have shown that bitumen recovery was less sensitive to temperature variations above 50°C but depression of bitumen recovery is favoured below 50°C for some ores tested.

6.2 Claims from this Research Work

1. The doping test and the visualization technique are good tools in helping to study the mechanisms of depression of bitumen recovery from poor processing ores.

2. Our study shows that in the presence of calcium or magnesium ions and fine clays doped to poison good processing ores, calcium ions act as bridge being adsorbed on clay and on bitumen through its carboxylic groups of natural surfactants.
3. A slime coating of hydrophilic montmorillonite clays is triggered by calcium ions and it is bound to bitumen surface. This results in the loss of bitumen hydrophobicity that is shown by a reduction of receding contact angle.
4. We have established a good correlation with bitumen recovery and receding contact angle showing that any effect that increase the contact angle will increase bitumen recovery.
5. The loss of bitumen hydrophoby will results in weaker attachment of bitumen to air bubbles and in decrease of bitumen floatability in water. Depression of bitumen recovery is then similar to the depression of bitumen from poor processing ores.
6. The visualization technique allows to identify poorer loads of bitumen on the surface of air bubbles during flotation for depressed bitumen recovery conditions.
7. We have found that montmorillonite clay and the smectite clay groups are clays that cause depression of bitumen recovery but not kaolinite or illite clays. We suggest that the depressing effect is due to the inherent characteristics of montmorillonite clay that differ from kaolinite and illite. Montmorillonite clay is characterized with large specific surface area provided for adsorption, strong affinity and favorable adsorption capacity for metal ions.
8. Zeta potentials measurements for all species tested, AFM studies and induction time are all excellent tools helping to elucidate the mechanisms of depression of bitumen recovery in presence of montmorillonite clays and calcium ions additions.

9. Magnesium and calcium ions at 1 molar concentration showed similar detrimental effect on bitumen recovery. This finding suggests that depression depends on valence and not on type of cations in water.
10. The effect of sodium is marginal below 1000 ppm concentration in water when montmorillonite was present. This finding suggests that the ionic strength of the slurries alone cannot be used to explain the observed depression of bitumen recovery.
11. The depression of bitumen recovery by increased calcium and magnesium ion concentrations in commercial process water would happen for ores containing a substantial amount of smectite fine clays.
12. Caustic addition would restore bitumen recovery from depression for good processing ores but not for poorly processing ores.
13. Sodium bicarbonate ($NaHCO_3$) addition will acts as good scavenger if added prior to conditioning but it cannot restore depression of bitumen once fully depressed.
14. High energy to the oil sands ore will improve recovery but low energy will favor depression of bitumen recovery.

6.3 Suggestions for Future work

1) To improve bitumen recovery from real poor processing ores, our findings suggest to soften water by precipitating calcium with sodium bicarbonate and to prevent clays from interacting with metal ions in water.
2) There is still a need to improve blending techniques that helps to dilute fines from poor processing ores and to allow synergy of good processing ore to trigger improved bitumen recover results.

3) It is important to establish the effect of energy in breaking and slurring clay lumps into fines that decrease bitumen recovery.

6.3.1 Effect of Air Injection

There is need to modify the unit cell to study the effect of air addition during flotation on the selectivity of flotation.

6.3.2 Visualization Technique and Factorial Design

1) Use the doping tests and visualization technique to study the effect of more other variables of Table 1-1 that affect mechanisms of depression of bitumen recovery.
2) Develop the visualization technique for use in commercial plant during the early stage of conditioning as a tool for detection of change of the incoming ore before reaching the extraction process, to evaluate synergetic effect obtained with blending and as a tool to detect loss of hydrophoby by change in the load of bitumen on air bubble surfaces.

REFERENCES

1. Adamson, A. W.:" Physical Chemistry of Surfaces", Fifth Edition, John Wiley & Sons, Inc., Chap. III, 53-105.
2. Agar, G.E., R. Stratton-Crawley and T.J. Bruce:" Optimizing the Design of Flotation Circuit", CIM Bulletin, Vol.**73**, 173-181, 1980.
3. Alberta Energy: "Oil Sands Facts", Alberta Department of Energy, 2002.
4. Albian Sands Energy Inc.: "Froth Treatment", 2001.
5. Alvarez, J., S.H. Castro and P. Carter:" A Characterization of the Flotation Rate of Coarse and Fine Molybdenite", Froth Flotation, S.H. Castro and J. Alvarez (Eds), Elsevier, Vol. **9**, 97-109, 1988.
6. Aplan F. F.:" Coal Flotation", A.M Gaudin Memorial Vol., M.C. Fuerstenau, American Institute of Mining, Metallurgical and Petroleum Engineers Inc., Vol. **2**, Chap. 45, 1235-1264, 1966.
7. Aplan, F.: "The Historical Development of Coal Flotation in the United States", In: Parekh, B.K., Miller, J.D. (Eds), Advances in Flotation Technology. SME, Littleton, CO, pp. 269-287, 1997.
8. Arbiter N.:"Flotation", SME Mineral Processing Handbook, N. L Weiss, American Institute of Mining, Metallurgical and Petroleum Engineers Inc., Vol. **1**, Section 5, pp 5-41 to 5-50, New York, 1985.
9. Arnold, B.J. and F. Aplan:" The Effect of Clay Slimes on Coal Flotation: Part I. The Nature of the Clay", Int. J. Miner. Process, Vol. **17**, 225-242, 1986.

10. Arnold, B.J. and F. Aplan:" The Effect of Clay Slimes on Coal Flotation: Part II. The Role of Water Quality", Int. J. Miner. Process, Vol. **17**, 243-260, 1986.

11. Ata S. and G.J. Jameson:" The Formation of Bubble Clusters in Flotation Cells ", Int. J. Miner.Process, Vol. **76**, pp 123-139, 2005.

12. Ball, M.W.: "Athabasca Oil Sands: Apparent Example of Local Origin of Oil: Bull. Amer. Asso. Petroleum Geol., Vol. **19**, 153-171, 1935.

13. Baptista M.V.: "Role of the Exchangeable Cations of Oil Sand Clays in Oil Sand Processing- Part **1**. Batch Tests", AOSTRA J. Res, Vol. **5**, 237-241, 1989.

14. Baptista, M.V. and C.W. Bowman:"The Flotation Mechanism of Solids from the Athabasca Oil Sands", Preprint,19th Can. Chem. Eng. Conf., Edmonton, 13pp, 1969.

15. Baptista, M.V.: "Role of the Exchangeable Cations and Iron-amorphous Coatings of the Oil Sand Solids in Oil Sand Processing- Part **2**. Pilot and Plant Tests." AOSTRA J. Res, Vol. **5**, 243-256, 1989.

16. Bara, B. and J. Masliyah:" Pipeline Digestion Modeling", Syncrude R&D Technical Seminar, Edmonton, Alberta, 1997.

17. Barrera-Godinez, J.A. and J.L. Watson: "A Procedure to determine Froth Flotation Kinetic Data using Computer Data Acquisition and Analysis", SME Annual Mtg., Salt Lake City, Utah, Prep. 90-60, Feb. 26-March 1, 1990.

18. Basu, S., K. Nandakumar and J. Masliyah: "A Study on Oil Displacement on Model Surfaces", J. Colloid Interface Sci., Vol. **182**, 82-94, 1996.

19. Basu, S., K. Nandakumar and J. Masliyah: "A Visual Study of High Grade Oil Sand Disintegration Process", J. Colloid Interface Sci., Vol. **205**, 201-203, 1998a-c.

20. Basu, S., K. Nandakumar, S. Lawrence and J. Masliyah:"Effect of Calcium Ion and Montmorillonite Clay on Bitumen Displacement by Water on a Glass Surface" Fuel, 2003.

21. Basu, S., Kanda, W. C., Nandakumar, K. and J. Masliyah: "The Effect of Hydrophobic and Hydrophilic Clays on Bitumen Displacement by Water on a Glass Surface", Ind. and Eng. Chem. Res., Vol. **37**, 959-965, 1998a-c.

22. Basu, S., Nandakumar, K. and J. Masliyah: "Effect of NaCl and MIBC/Kerosene on Bitumen Displacement by Water on a Glass Surface", Colloids Surf. A **136**, 71-80, 1998-b.

23. Basu, S., Nandakumar, K. and J. Masliyah: "A Model for Detachment of a Partially Wetting Drop from a Solid Surface by Shear Flow", J. Colloid Interface Sci., Vol. **190**, 253-257, 1997b.

24. Basu, S., Nandakumar, K. and J. Masliyah:"A Study on Daughter Droplet Formation in Bitumen/Glass/Water Contact Displacement due to Instability", Fuel, Vol.**79**, 837-841, 2000.

25. Basu, S., Nandakumar, K. and J. Masliyah: "A Study on Oil Displacement on Model Surfaces", J. Colloid Interface Sci., Vol. **182**, 82-84, 1996.

26. Basu, S., Nandakumar, K. and J. Masliyah: "On Bitumen Liberation from Oil Sands", Can. J. Chem. Eng., Vol. **75**, 196-204, 1997a.

27. Bensebaa, F., L.S. Kotlyar, B.D. Sparks, and K.H. Chung:" Organic Coated Solids in Athabasca Bitumen: Characterization and Process Implications", Can. J. Chem. Eng, 610-616, 2000.

28. Bichard, J.A.: “Oil Sands Composition and Behavior Research”, the research papers of John A. Bichard (1957-1965), AOSTRA technical series, Vol. **4**, Edmonton, 1987.

29. Bolt, G.H., M.G.M. Bruggenwert and A. Kamphorst:” Adsorption of Cations by Soil”, In: G.H. Bolt and, M.G.M. Bruggenwert (Editors), Soil Chemistry, A. Basic Elements, Elsevier, Amsterdam, New York, N.Y., 54-90, 1976.

30. Bonifazi, G., P. Massacci and A. Meloni: “3D Froth Surface Rendering and Analysis Technique to Characterize Flotation Processes”,Int.J.Min.Proc,Vol.**64**,153-161, 2002.

31. Bowman, C.W.: “Molecular and Interfacial Properties of Athabasca Tar Sands”, Proc. 7th World Petrol. Congr. Vol. **3**, 583-604, 1967.

32. Brown, D.J. and H.G. Smith:” Continuous Testing of Frothers”, Colliery Eng., 31, 245-250, 1954.

33. Bulmer J. T. and J. Starr:” Syncrude Analytical Methods for Oil Sand and Bitumen Processing”, Syncrude Research, AOSTRA, 1-20, 20-75, 1979.

34. Burdon, R.G., R.W. Booth and S.K. Mishra:” Factors Influencing the Selection of Processes for the Beneficiation of Fine Coal”, Proc. Seventh Int. Coal Preparation Congr., Australia, 25 pp., 1976.

35. Cameron Engineers: “Oil Sands”, Synthetic Fuels Data Handbook, 2nd Ed., Cameron Engineers Inc., Colorado, USA, 1978.

36. Camp, F.W.: “Processing Athabasca Tar Sands – Tailings Disposal”, Can. J. Chem. Eng., Vol. **55**, 581-591, 1977.

37. Camp, F.W.: “The Tar Sands of Alberta, Canada”, 3rd ed., Cameron Engineers Inc., Colorado, 1976.

38. Carroll, B.: “The Direct Study of Oily Soil Removal from Solid Substrates in Detergency”, Colloids Surf. A. Vol. **114**, 161-164, 1996.

39. Chen, F., J.A. Finch, Z. Xu and J. Czarnecki: “Wettability of Fine Solids Extracted from Bitumen Froth”, J. Adhesion Sci. Technol., Vol. **13**, 1209-1224, 1999.

40. Cho, Y.S. and J.S Laskowski:” Effect of Flotation Frothers on Bubble Size and Foam Stability”, Int. J. Miner. Process. Vol. **64,** 69-80, 2002.

41. Chow, R.S. and K. Takamura: “Electrophoretic Mobilities of Bitumen and Conventional Crude-in-Water Emulsions Using the Laser Doppler Apparatus in the Presence of Multivalent Cations”, J. of Colloid and Interface Sci., Vol. **125**, No. **1**, 212-225, September 1988.

42. Clark, K. A.: “Athabasca Oil Sands – Fundamentals Affecting Development”, Can. Pet., **7**, 18-21, 1966.

43. Clark, K. A.: “Hot-Water Separation of Alberta Bituminous Sand”, Trans. Can. Inst. Min. Metal., Vol. **47**, 257-274, 1944.

44. Clark, K. A.: “The Hot Water Washing Method for Recovering of Oil from the Alberta Tar Sands”, Can. Oil Gas Ind., Vol. **3**, 46-50, 1950.

45. Clark, K.A. and D.S. Pasternack: "Hot Water Separation of Bitumen from Alberta Bituminous Sand”, Ind. Eng. Chem., Vol. **24**, 1410-1416, 1932.

46. Clark, K.A.: “The Separation of the Bitumen from Alberta Bituminous Sands”, Can. Inst. Min. Metal. Bull. Vol. **22**, 1385-1395, 1929.

47. Clift R., J.R. Grace and M.E. Weber: “Bubbles, Drops and Particles”, Academic Press, New York, 1978.

48. Cottrell, J.H., "Development of an Anhydrous Process for Oil Sand Extraction", K.A. Clark Vol., Alberta Research Council, Edmonton, Alberta, 193-206, 1963.

49. Cox, Doug: "Suncor Experiences: Sinking Bitumen, High Chloride Concentration, Type X Ore, High Fines Ore, Oxidized Ore, and Hard Ore", CONRAD Seminar, Fort McMurray, 2000.

50. Cuddy, G.: "Empirical Studies on the Relationship between Process Water Chemistry and Oil Sands Processability (Syncrude Canada Ltd.)", CONRAD Seminar, Fort McMurray, 2000.

51. Currie, D.J., A.P. Hathaway, E.E. Isaacs, A. Mar, D.N. Morrison and C. Richmond: "The Potential of the Crumble Tests as a Tool for Oil Sands Research", in "30th Can. Chem. Eng. Conference, Vol. IV: Oil Sands, Coal and Energy Modeling", S.E.Wanke (Ed.), Edmonton, Alberta, 1125-1142, 1980.

52. Cymerman G., A. Leung, W. Maciejewski, J. Spence and B. McDonald: " Oil Sand Hydrotransport Tests at Syncrude Canada Ltd.", 18th International Conference on Coal Utilization & Slurry Technologies, Clearwater, Florida, April 26-29, 1993.

53. Cynthia P. and R St. C. Smart:" Statistical Comparison of Hydrophobic and Hydrophilic Species on Galena and Pyrite Particles in Flotation Concentrates and Tails from TOF-SIMS Evidence", Int. J. Miner. Process, Vol. **64**, 43-54, 2002.

54. Dabros T., Q. Dai, H. Hamza and J. Czarnecki, J. S. Laskowski and G. W. Poling, "Processing of Hydrophobic Minerals and Fine Coal", CIM, pp. 413-424, 1995.

55. Dai, Q. and K. Chung, Fuel, Vol. **74**, 1858-1864, 1995.

56. Dai, Qi, and K.H. Chung: "Trona (Mineral Grades Sodium Carbonate) as a Process Aid for the Hot Water Process", J. of Can. Petr. Tech., Vol. **35**, no **1**, January 1996.

57. Dai, Q., K.H. Chung and J. Czarnecki:"Formation of Calcium Carbonate in the Bitumen/Aqueous Sodium Hydroxide System",AOSTRA J.Res,Vol. **8**, 95-101, 1992.

58. Darcovich, K., L.S. Kotlyar, W.C. Tse, J.A. Ripmeester, C.E. Capes, and B.D. Sparks:"Wettability Study of Organic Rich Solids separated from Athabasca Oil Sands", Energy and Fuels, 386,1989.

59. Drelich, J., and Miller, J. D.:"SME Annual Meeting, Denver, Colorado",95-11, 1995.

60. Drelich, J., and Miller, J. D.: "Surface and Interfacial Tension of the Whiterocks Bitumen and its Relationship to Bitumen Release from Tar Sands during Hot Water Processing", Fuel, Vol. **73**, 1504-1510, 1994.

61. Ducker, W.A., Z. Xu, D.R. Clarker and J.N. Israelachvili: "Forces between Alumina Surfaces in Salt Solutions Non-DLVO Forces and the Implications for Colloidal Processing", J. Am. Ceram. Soc, Vol.**77**, 437-43,1994.

62. Eskin D., Y. Leonenko, S. Lezhnin and O. Vinogradov: "A Model of Oil Sand Lump Digestion", Miner Eng., Vol. **15**, 469-472, 2002.

63. Ewing, G. W.:" Instrumental Methods of Chemical Analysis", McGrow-Hill Kogakusha, Ltd., Chap. 25, 513-522, 1960.

64. Finch, J.A and G.S. Dobby: " Column Flotation", Pergamon Press, 1990.

65. Finkelstein N. P. and S. A. Allison:" The Chemistry of Activation, Deactivation and Depression in the Flotation of Zinc Sulfide: A review", Flotation A. M. Gaudin Memorial, Vol. **1**, AIME, Chap. 14, 416, 1976.

66. Fitzgerald J.J.: "Black Gold with Grit", Evergreen Press Ltd., Vancouver, Canada, 264pp, 1978.

67. Flynn, M., B. Bara, J. Czarnecki and J. Masliyah: "An Investigation of the Effect of Air Addition during Oil Sand Conditioning", Can. J. Chem. Eng., Vol. **79**, Number 3, 468-470, 2001.
68. FTFC (Fine Tailings Fundamentals Consortium):" Advances in Oil Sands Tailings Research", AOSTRA Oil Sands and Research Division, Edmonton, 1995.
69. Fuerstenau, M. C., J.D. Miller and M.C. Kuhn:"Chemistry of Flotation", AIME Society of Mining Engineers, New York, 1985.
70. Fuerstenau, M.C.:"Flotation", A. M. Gaudin Memorial Vol. **1**,AIME, chap.3-6, 1976.
71. Fujimoto Takehiko: "New Introduction to Surface Active Agents", Sanyo Chemical Industries, LTD., 20-22, 1985.
72. Gaudin, A. M.:" Flotation", McGrow-Hill Book Co. Inc., Chap. 11, 1957.
73. George, R.L.: "Mining for Oil", Scientific American, 84-85, March 1998.
74. Gu, G., Z. Xu, K. Nandakumar and J. H. Masliyah: "Effects of Physical Environment on Induction Time of Air-Bitumen Attachment", Int. J. Miner. Proc. Vol. **69**, 2003-b.
75. Guarini, M., J. Caceres, A. Guesalaga, A. Cipriano, J. Olmedo, and H. Lozano: " A Sensor for assessing the Quality of the Mineral Flotation Process", Proc. IEEE Int. Symp. On Industrial Electronics, Santiago, Chile, 386-391, 1994.
76. Hall, A.C., S.H Collins, and J.C. Melrose: "Stability of Aqueous wetting Films in Athabasca Tar Sands", Soc. Petrol. Eng. J., 249-258, April 1983.
77. Happel, J. and H. Brenner: "Low Reynolds Number Hydrodynamics with Special Applications to Particulate Media", Noorhohh, Leiden (2nd ed.), Ch. 7., 1973
78. Healy, T.W. and L.R. White: "Ionizable Surface Group Models of Aqueous Interfaces", Adv. Colloid Interface Sci., Vol. **9**, 303-345, 1978.

79. Hepler, L.G. and C. Hsi: "AOSTRA Technical Handbook on Oil Sands, Bitumen and Heavy Oils", Series 6, Edmonton 1989.

80. Hepler, L.G. and R.G. Smith: "The Alberta Oil Sands: Industrial Procedures for Extraction and Some Recent Fundamental Research", Series 14, Edmonton 1994.

81. Holtham, P. N. and K.K. Nguyen: "On-line Analysis of Froth Surface in Coal and Mineral Flotation Using JKFrothCam", Int. J. Miner. Proc., Vol. **64**,163-180, 2002.

82. Horsley, R. M., and H. G. Smith:" Principles of Coal Flotation", Fuel, London, Vol. **1**, 54-63, January 1956.

83. Hupka, J., A.G. Oblad and J.D. Miller: "Diluent-Assisted Hot-Water Processing of Tar Sands", AOSTRA J. Res, Vol. **3**, 95-102, 1987.

84. Innes, E.D. and Fear, J.V.D.:" Canada's first Commercial Tar Sand Development, in "7th World Petroleum Congress", Elsevier, Mexico, 633-650, 1967.

85. Itokumbul, M.T., N. Kosaric, W. Bulani and W.L. Cairns: "Froth Flotation for the Beneficiation of Heavy Minerals from Oil Sand Tailings", AOSTRA J. Res., Vol. **2**, 59-66, 1985.

86. Jameson G. J.: "Physical Aspects of fine Particle Flotation", Principles of Mineral Flotation, Australian Institute of Mining and Metallurgy, pp 223-224, Australia 1984.

87. Jowett, A., H. El-Sinbawy and H.G. Smith: "Slime Coating of Coal in Flotation Pulps", Fuel, Vol. **35**, 303-309, 1956.

88. Kappl, M. and H.J. Butt, "The Colloidal Probe Technique and its Application to Adhesive force Measurements", Particle and Particle Systems Characterization, Vol.**19**, 129-143, 2002.

89. Kasongo, T. Z.A. Zhou, Z.Xu and J. Masliyah: "Effect of Clays and Calcium Ions on Bitumen Extraction from Athabasca Oil Sands Using Flotation", 49th Canadian Chemical Engineering Conference, Saskatoon, October 3-6, 1999.

90. Kasongo, T., Z. A. Zhou, Z. Xu and J. H. Masliyah: "Effect of Calcium Ions and Fine Clays on Bitumen Extraction from Athabasca Oil Sands Using Flotation", Can. J. Chem. Eng., Vol. **78**, 674-681, 2000.

91. Kasongo, T.: "Effect of Metal Ions and Clays on Flotation of Bitumen during Hot Water Extraction Process", CONRAD Seminar, Fort McMurray, 2000.

92. Kasperski, K. L.: ", Review of Research on Aqueous Extraction of Bitumen from Mined Oil Sands", CANMET, Report CWRC 01-17 (CF), 67 pp., 2001.

93. Kasperski, K.: "A Review of Properties and Treatment of Oil Sands Tailings", AOSTRA J. Res., Vol. **8**, 11-15.

94. Kessick, M.:" Clay Slimes from the Extraction of Alberta Oil Sands, Florida Phosphate Matrix and other Mined Deposits", CIM Bulletin, 80-88, February 1978

95. Klassen, V.I. and Mokrousov, V.A.: "An Introduction to the Theory of Flotation", Engl. Transl. by J. Leja and G.W. Poling, Butterwoths, London, 1963.

96. Kotlyar, L.S. and B.D. Sparks: "Isolation of Inorganic Matter-Humic Complex from Athabasca Oil Sands", AOSTRA J. Res., Vol. **2**, 103-111, 1985.

97. Kotlyar, L.S., H. Kodama, B.D. Sparks, and P.E. Grattan-Bellew:" Non-Crystalline Inorganic Matter-Humic Complexes in Athabasca oil Sands and their Relationship to Bitumen Recovery", Applied Clay Science **2**, 253- 271, 1987a.

98. Kotlyar, L.S., J.A. Ripmeester and B.D. Sparks: "Comparative Study of Organic Rich Solids Present in Utah and Athabasca Oil Sands, In "The Future of Heavy Crude and Tar Sands", UNITAR, Paper No. 16, Preprint 1, p.10, 1988.

99. Kotlyar, L.S., J.A. Ripmeester, B.D. Sparks, and D.S. Montgomery: " Characterization of Organic Rich Solids Fractions isolated from Athabasca Oil Sands Using a Cold Water Agitation Test", Fuel **67** (2), 221, 1987b.

100. Kotlyar, L.S., J.A. Ripmeester, B.D. Sparks, and D.S. Montgomery:" Characterization of Oil Sands Solids closely associated with Athabasca Bitumen", Fuel **67**, 808- 814, 1988.

101. Kotlyar, L.S., Sparks, B.D. and H. Kodama:"Some Chemical and Mineralogical Properties of Fine Solids Derived from Oil Sands", AOSTRA J. Res., Vol. **1**, 99-106, 1984.

102. Lam, C.N.C., R. Wu, D. Li, M.L. Hair and A.W. Neumann: "Study of the Advancing and Receding Contact Angles: Liquid sorption as a cause of Contact Angle Hysteresis", Advanced in Colloid and Interface Sci., Vol. **96**, 169-191, 2002.

103. Laskowski, J.: "Particle-bubble Attachment in Flotation", Minerals Sci. Eng, Vol. **6**, no. 4, 223-235, 1974.

104. Leja, J and C.W. Bowman:" Application of Thermodynamics to Athabasca Tar Sands", Can. J. Chem. Eng., Vol. **46**, 479-481, 1968.

105. Liu J., Z. Xu and J. Masliyah:" Interaction between Bitumen and Fines in Oil Sands Extraction System: Implication to Bitumen Recovery", Can. J Chem. Eng., Vol. **82**, 655-666, 2004.

106. Liu, J. and Z. Xu:" The Bitumen/Clays Interactions Interpreted by Zeta Potential Measurement", NSERC /Syncrude Review Meeting, Edmonton, Alberta, , 2001.

107. Lynch, A. J., N.W. Johnson, E.V. Manlapig, and C.G. Thorne:" Mineral and Coal Flotation Circuits, Their Simulation and Control", Developments in Mineral Processing, 3, Elsevier Scientific Publishing Co., New York, 1981.

108. Malmberg, E.W, and R.M. Bean:" Hot Water Processing of Athabasca Oil Sands: II.Microscope Studies of the Conditioning Process", Amer. Chem. Soc. Div. Petrol. Chem. Preprints; American Chemical Society, San Francisco, F25-F37, 1968.

109. Malysa, K., S. Ng, J. Czarnecki, and J. Masliyah: "A Method of Visualization and Characterization of Aggregate Flow inside a Separation Vessel, Part 1. Size, Shape and Rise Velocity of the Aggregates", Inter. J. Miner. Pro., Vol. **55**, 171-188, 1999.

110. Malysa, K., S. Ng, J. Czarnecki, and J. Masliyah: "A Method of Visualization and Characterization of Aggregate Flow inside a Separation Vessel, Part 2. Composition of the Bitumen-Air Aggregates", Inter. J. Miner. Process, Vol. **55**, 189-202, 1999.

111. Masliyah J. H. and R. G. Murray: "Extraction and Upgrading of Oil sands Bitumen", Intensive Short Course, University of Alberta, Edmonton, 1999.

112. Masliyah J. H.: "Intensive Short Course: Extraction of Oil sands Bitumen", University of Alberta, Edmonton, Alberta, Canada, 2000.

113. Masliyah J. H.: "Intensive Short Course: Extraction of Oil sands Bitumen", University of Alberta, Edmonton, Alberta, Canada, 2003.

114. Masliyah, J., Z. Zhou, Z. Xu, J. Czarnecki and H. Hamza: "Understanding Water-Based Bitumen Extraction from Athabasca Oil Sands", Can. J Chem. Eng., 82, 628-654, 2004.

115. Masliyah, J.H., R. Jauhari and M.R. Gray: "Drag Coefficient for Air Bubbles Rising along an Inclined Surface", Chem. Eng. Sci., Vol. **49**(12), 1905-1911, 1994.

116. Masliyah, J.H., R. Jauhari and M.R. Gray: "Rising Velocities of Air Bubbles along an Inclined Surface", in: "Advances in Engineering and Fluid Mechanics, Mixed-Flow Hydrodynamics", Chap. 25, N.P.Cheremisinoff, Ed., Gulf Publ. Co., Houston, TX, 581-602, 1996.

117. Masliyah, J.H., Z. Zhou, Z. Xu, J. Czarnecki and H. Hamza: "Understanding Water-Based Bitumen Extraction from Athabasca Oil Sands", submitted for publication to Can. J. Chem. Eng., August, 2003.

118. Masliyah, J.H.: "Electrokinetic Transport Phenomena", AOSTRA Technical Publication Series **12**, Alberta, 1994.

119. Masliyah, J.H.: "Bitumen Extraction", Extraction and Upgrading of Oil Sands Bitumen, Intensive Short Course, Keyano College, Fort McMurray, Alberta, 2003.

120. Mathieson, D. and D. Stenason: "Investing in Oil sands", Scotia Capital, the Drill Bit, May 2001.

121. Mishra, S.K.:" The Slime Problem in Australian Coal Flotation", Australasian I.M.M., Mill Operators Conference, Mt. Isa, 159-168, 1978.

122. Montgomery, D.C. and G. C. Runger: "Applied Statistics and Probability for Engineers", John Wiley & Sons, Inc., chap. 12, 686-801, 1994.

123. Montgomery, D.C.: "Design and Analysis of Experiments", John Wiley & Sons, Inc., Fourth Edition, chap. 6, 228-289, 1996.

124. Moolman, D.W., J.J. Eksteen, C. Aldrich, and J.S.J. van Deventer: "The Significance of Flotation Froth Appearance for Machine Vision Control", Int. J. Miner. Process, Vol. **48**, 135-158, 1996.

125. Morgan, G.: "An Energy Renaissance in Oil Sands Development", World Energy, **4**, 46-53, 2001.

126. Morrison, I. D. and S. Ross: "Colloidal Dispersions. Suspensions, Emulsions and Foams", Wiley Interscience, 316-352, 2002.

127. Moschopedis, S.E., J.F. Fryer and J.G. Speight: "Water-Soluble Constituents of Athabasca Bitumen", Fuel, **56**, 109-110, 1977.

128. Moschopedis, S.E., K.F. Schulz, J.G. Speight, and D.N. Morrison: "Surface-Active Materials from Athabasca Oil Sands", Fuel Process. Technol., **3**, 55-61, 1980.

129. Mossop, G. D.: "Geology of the Athabasca Oil Sands", Science, **207**, 145-152, 1980.

130. Nasr, Tawfik, N.: "Steam Assisted Gravity Drainage (SAGD). A New Oil Production Technology for Heavy Oil and Bitumen", Alberta research Council, Calgary, Canada, 2003.

131. Ng, S., P. Warszynski, M. Zembala and K. Malysa: "Bitumen-Air Aggregates Flow to Froth Layer: I. Method of Analysis", Minerals Eng., Vol. **13** (14-15), 1505-1517, 2000.

132. Ng, S., P. Warszynski, M. Zembala and K. Malysa: "Bitumen-Air Aggregates Flow to Froth Layer: II. Effect of Ore Grade and Operating Conditions on Aggregate Composition and Bitumen Recovery", Minerals Eng., Vol. **13** (14-15), 1519-1532, 2000.

133. O'Carroll, Josephine B.: "Factors Affecting Bitumen Recovery from Oil Sands", M.A.Sc. Thesis, University of Ottawa, 2000.

134. Osipow, L.I.:" Surface Chemistry, Theory and Industrial Applications", American Chemical Society Monograph Series, Reinhold Publishing Corporation, New York, 7-10, 70-71, 80, 1962.

135. Paul, A.H.: "Muskeg River Mine Ore Reserve Report – 2002", Chief Mine Geologist, Albian Sands Energy Inc., report # 254-2, 4 February 2003.

136. Poling G. W. and M. J. V. Beattie:" Selective Depression in Complex Sulfide Flotation", Principles of Mineral Flotation, The Wark Symposium, The Australian Institute of Mining and Metallurgy, 137-138, Victoria, Australia, 1984.

137. Rabinovich, Y.I. and R.H. Yoon: "Use of Atomic Force Microscope for the Measurements of Hydrophobic Forces between Silanated Silica Plate and Glass Sphere"', Langmuir, Vol.**10**, 1903-1909, 1994

138. Raghavan S. and D. W. Fuerstenau:" On the Wettability and Flotation Concentration of Submicron Hematite Particles with Octylhydroxamate as Collector", Advances in Interfacial Phenomena, AICHE Symposium. Series, Vol. **71**, 59-67, 1975.

139. Rouquerol, F., J. Rouquerol and K. Sing: "Adsorption by Powders and Porous Solids", Academic Press, 355-361, London 1999.

140. Rowe, A.W., R.M. Counce, S.A. Morton III, M. Hu and W. DePaoli: "Oil Detachment from Solid Surfaces in Aqueous Surfactant Solutions as a Function of pH", Ind. Eng. Chem. Res., Vol. **41**, 1787-1795, 2002.

141. Sanford, E.C. and F.A. Seyer: "Processabilty of Athabasca Tar Sand Using a Batch Extraction Unit: The Role of NaOH", CIM Bulletin, 164-169, March 1979.

142. Sanford, E.C.:" Processability of Athabasca Oil Sand: Interrelationship between Oil Sand Fine Solids, Process Aids, Mechanical Energy and Oil Sand Age after Mining", Can. J. Chem. Eng., Vol. **61**, 554-567, 1983.

143. Schramm, L.L, R.G. Smith and J.A. Stone:" A Surface-Tension Method for the Determination of Anionic Surfactants in Hot Water Processing of Athabasca Oil Sands", Colloids and Surfaces, Vol. **11**, 247-263, 1984.

144. Schramm, L.L, R.G. Smith and J.A. Stone:" On the Processability of Mixtures of Oil Sands", AOSTRA J. Res, Vol. **I**, No. **3**, 147-161, 1985.

145. Schramm, L.L, R.G. Smith and J.A. Stone:" The Influence of Natural Surfactant Concentration on The Hot Water Process for Recovering Bitumen from the Athabasca Oil Sands", AOSTRA J. Res, Vol. **I**, 5-14, 1984.

146. Schramm, L.L. and R.G. Smith: "The Influence of Natural Surfactants on Interfacial Charges in the Hot-Water Process for Recovering Bitumen from the Athabasca Oil Sands", Colloids and Surf, Vol. **14**, 67-85, 1985.

147. Schramm, L.L. and R.G. Smith: "Some Observations on the Ageing Phenomenon in the Hot Water Processing of Oil Sands. Part 1. The Nature of the Phenomenon", AOSTRA J. Res., Vol, **3**, 215-224, 1987-b

148. Schramm, L.L. and R.G. Smith: "Some Observations on the Ageing Phenomenon in the Hot Water Processing of Oil Sands. Part 2. The Reversibility of the Phenomenon", AOSTRA J. Res., Vol. **3**, 195-214, 1987-c.

149. Schramm, L.L. and R.G. Smith: “Two Classes of Anionic Surfactants and Their Significance in Hot Water Processing of Oil Sands”, Can. J. Chem. Eng., Vol. **65**, 799-811 1987-a.

150. Schramm, L.L. and R.G. Smith:” The influence of Mineral Components on the Generation of Natural Surfactants from Athabasca Oil Sands in the alkaline Hot-Water Process”, Fuel Processing Technology, **30**, 1-14, 1992.

151. Schramm, L.L., R.G. Smith, and J.A. Stone: “On the Processabilty of Mixtures of Oil Sands”, AOSTRA J. Res., Vol. **1**(3), 147-161, 1985.

152. Shaw D. J.: “Electrophoresis”, Academic Press, 1-28, London 1969.

153. Shaw, D.J.: "Introduction to Colloid and Surface Chemistry”, Butterworth-Heinemann, 4th edition, Vol. **64-65**, 174-209, 1999.

154. Shaw, R. C., J. Czarnecki, L. Schramm and D. Axelson: “Bituminous Froths in the Hot-Water Flotation Process”, in “Foams: Fundamentals and Applications in the Petroleum Industry”, Schramm, L.L. ed., Elservier, Washington, D.C., 423-459, 1994.

155. Shaw, R. C.: “Subsampling Bulk Quantities of Oil Sand for Oil, Water, and Solids”, Alberta Committee on Oil Sands Analysis Workshop, Lake Louise, , 1983.

156. Smith, R.G. and L.L. Schramm: “The Influence of Mineral Components on the Generation of Natural Surfactants from Athabasca Oil Sands in the Alkaline Hot Water Process”, Fuel Process. Technol. **30**, 1-14, 1992.

157. Somasundaran, P. and A. Luo: “Oxide Mineral Flotation Fundamentals”, in: “Advances in Flotation Technology”, B.K. Parekh and J.D. Miller eds., Society for Mining, Metallurgy, and Exploration, Inc., Denver, CO, 23-43, 1999.

158. Somasundaran, P.: “Interfacial Chemistry of Particulate Flotation”, Advances in Interfacial Phenomena, AICHE Symposium. Series, Vol. **71**, 1-15, 1975.

159. Sparks, B.D., L.S. Kotlyar, J.B. O’Carroll, and K.H. Chung: “Athabasca Oil Sands: Effect of Organic Coated Solids on Bitumen Recovery and Quality”, J. of Petroleum Science and Engineering, Vol. **1086**, 1-14, 2003.

160. Speight, J.G. and S.E. Moschopedis: “Factors Affecting Bitumen Recovery by the Hot Water Process”, Fuel Process. Technol., **1**, 261-268, 1977.

161. Starkweather, B.A., R.M. Counce and X. Zhang: “Displacement of a Hydrocarbon Oil from a Metal Surface Using a Surfactant Solution”, Sep. Sci. Technol., Vol. **34**, 1447-1462, 1999.

162. Starkweather, B.A., X. Zhang and R.M. Counce: “An Experimental Study of the Change in the Contact Angle of an Oil on a Solid Surface”, Ind. Eng. Chem. Res., Vol. **39**, 362-366, 2000.

163. Subrahmanyam, T.V., M.B. M. Monte, A. Middea, E. Valdiviezo and F.F. Lins:” Contact Angles of Quartz by Capillary Penetration of Liquids and Capture Bubble Techniques”, Minerals Engineering, Vol. **12**, No. 11, 1347-1357, 1999.

164. Sutherlan, K.L. and I.W. Wark: “Principles of Flotation”, Aust. Inst. of Mining and Metallurgy Inc., 38-49, Melbourne 1955.

165. Takamura, K. and D. Wallace: "Experimental and Theoretical Studies of the Hot Water Processability of Different Grades of Athabasca Oil Sands", in “Flocculation in Biotechnology and Separation Systems”, Y.A. Attia, Ed., Elsevier ,579-597, 1987.

166. Takamura, K. and D. Wallace: "The Physical Chemistry of the Hot Water Process, The J. of Canadian Petroleum Technology, Vol. **27**, No. 6, 98-106. Nov-Dec 1988.

167. Takamura, K. and R.S. Chow: "The Electric Properties of the Bitumen/Water Interface, Pt II, and Application of the Ionizable Surface-Group Model", Colloids and Surf, Vol. **15**, 35, 1985.

168. Takamura, K. and R.S. Chow: "A Mechanism for Initiation of Bitumen Displacement from Oil Sand", Canadian J. of Petroleum Technology, Vol. **22**, 22-30, Nov-Dec., Montreal 1983.

169. Takamura, K., R.S. Chow and D.L. Tse: "The Prediction of Electrophoretic Mobilities and the Coagulation Behavior of Bitumen-in-Water Emulsions in Aqueous NaCl and CaCl2 Solutions Using Ionizable Surface-Group Model", Proceedings of the Symposium on Flocculation in Biotechnology and Separation Systems, San Francisco, CA, July 1986.

170. Takamura, K.: "Microscopic Structure of Athabasca Oil Sand", the Canadian J. of Chemical Engineering, Vol. **60**, 538-545, August 1982.

171. Tato, T. and R. Ruch: "Stabilization of Colloidal Dispersions by Polymer Adsorption", Marcel Dekker, Inc., Surfactant Sci. Series, Vol. **9**, 41-63.

172. The Fine Tailings Fundamentals Consortium (FTFC): "Advances in Oil Sands Tailings Research", Alberta Department of Energy, Oil Sands and Research Division, Publisher, 1995.

173. Thimm, H.F.:"Dependence of some SAGD Operations Characteristics on Stream Zone Pressure", Thimm Engineering Inc., Calgary, Alberta, Canada, 2003.

174. Tipman, R.: "Muskeg River Pilot Plant: Experience with Poorly Processing Ores", in Problem Ores, CONRAD Seminar, Fort McMurray, 1, 2000.

175. University of Alberta: "Thesis Handbook; a Manual of Regulations and Guidelines for Thesis Preparation", University of Alberta 1999.

176. Van Olphen, H.: "An Introduction to Clay Colloid Chemistry", Second Edition, John Wiley and Sons, Inc., 56-76, 233-235, 1977.

177. Ventura-Medina, E. and J.J. Cilliers: "A Model to Describe Performance Based on Physics of Foams and Froth Image Analysis", Int. J. Min. Proc., Vol. **67**, 79-99, 2002.

178. Verwey, E.J.W. and J.Th. G. Overbeek: "Theory of the Stability of Lyophobic Colloids", New York, Elsevier Publishing Co., 1948.

179. Wallace D.:"Executive Summary", Report to Albian Sands, November 2003.

180. Wallace, D. and B. Kratochvil: "Sampling Uncertainty in the Determination of Major Components in Athabasca Oil Sand", AOSTRA J. of Research, Vol. **1**, 1981.

181. Wallace, D. and B. Kratochvil: "Use of a Mill and Spinning Riffle for Subsampling Laboratory Samples of Oil Sand", AOSTRA J. Res, Vol. **2**, Number 1, 37-45, 1985.

182. Wallace. D., Kadatz, B., Tipman, R. and S. Snaychuck: "Problem Ores: Application of BEU Units to the Simulation of Continuous Processes", CONRAD Oil Sands Extraction Fundamentals and Process Water Chemistry, Fort McMurray, AB, May 7-8, 2001.

183. Wang, W., Z. A. Zhou, K. Nandakumar, Z. Xu and J. Masliyah: "An Induction Time Model for the Attachment of an Air Bubble on a Hydrophobic Sphere in Aqueous Solutions" Int. J. Miner. Process, 2003-c.

184. Wang, W., Z. A. Zhou, K. Nandakumar, Z. Xu and J. Masliyah: "Attachment of Individual Particles to a Stationary Air Bubble in Model Systems", Inter. J. Miner. Process, Vol. **68**, 47-69, 2003-a.

185. Wang, W., Z. A. Zhou, K. Nandakumar, Z. Xu and J. Masliyah: "Effect of Surface Mobility on the Sliding of Glass Beads around a Bubble or Glass Sphere", J. Colloid Interface Sci. Vol. **259**, 81-88, 2003-b.

186. Wang, W., Z. A. Zhou, K. Nandakumar, Z. Xu and J. Masliyah: "Enhanced Surfactant Transfer under the Influence of Charged Colloidal Particles", J. Colloid Interface Sci., 2003-d.

187. Warren L. J.:" Ultra fine Particles in Flotation", Advances in Interfacial Phenomena, AICHE Symposium. Series, Vol. **71**, 190-191, 1975.

188. Wills, B. A.:" Mineral Processing Technology", 5th Ed., Pergamon Press, 1992.

189. Xu, M., P. Quinn and R. Stratton-Crawley:" A Fee-Line Aerated Flotation Column, Part 2: Modeling and Scale-up", Miner. Engineering, Vol. **9**, 655-666, 1996.

190. Xu, Z. and J. H. Masliyah: "Effect of Recycle Water from CT Process on Bitumen Recovery from Oil Sands", Progress Report #2, NSERC, 2001.

191. Xu, Z., J. Liu, J.W Choung, and Z. Zhou:" Electrokinetic Study of Clay Interactions with Coal in Flotation", Int. J. Miner. Process, Vol. **68**, 183-196, 2003.

192. Xu, Z.: "Surface Chemistry in Materials Processing", Course MATE 633, University of Alberta, Winter 2000.

193. Yang, C., T. Dabros, D. Li, J. Czarnecki, and J.H. Masliyah: "A Visualizing Method for Study of Micron Bubble Attachment onto a Solid Surface under Varying Physicochemical Conditions", Ind. Eng. Chem. Res., Vol.**39** (12), 4949-4955, 2000.

194. Zhou, Z. A., H. Hussein, Z. Xu, J. Czarnecki and J. H. Masliyah: "Interaction of Ionic Species and Fine Solids with a Low Energy Hydrophobic Surface from Contact Angle Measurement", J. Colloid. Interface Sci., Vol. **204**, 342-349, 1998.

195. Zhou, Z. A., T. Kasongo, Z. Xu and J. H. Masliyah: "Assessment of Bitumen Recovery from the Athabasca Oil Sands Using a Laboratory Denver Flotation Cell", Submitted to Can. J. Chem. Eng., 2003-b.

196. Zhou, Z. A., Xu, Z., Masliyah, J. H. and Czarnecki, J.: "Coagulation of Bitumen with Fine Silica in Model Systems", Colloids and Surfaces, Physicochemical. Eng. Aspects, Elsevier, Vol. **148**, 199-211, 1999.

197. Zhou, Z. A., Z. Xu and J. H. Masliyah: "Effect of Natural Surfactant Released from Athabasca Oil Sands on Gas Holdup in a Water Column", Can. J. Chem. Eng., Vol. **78**, 617-624, 2000-b.

198. Zhou, Z. A., Z. Xu and J. H. Masliyah: "Factors Affecting Bitumen Surface Hydrophobicity during Bitumen Extraction from Athabasca Oil Sands", 2003.

199. Zhou, Z. A., Z. Xu, J. Masliyah, T. Kasongo, T. Kizior and D. Cox: "Application of On-Line Visualization to Flotation Systems", Proceedings, CMP, Ottawa, Canada, Paper **7**, 119-137, 2000.

200. Zhou, Z., T. Kasongo, Z. Xu and J. Masliyah:" Assessment of Bitumen Recovery from the Athabasca Oil Sands using a Laboratory Denver Flotation Cell", Can. J. Chem. Eng., Vol. **82**, 696-703, 2004.

APPENDEX A1

A1-1 Atomic Force Microscopy (AFM technique), (Liu, 2003)

The laboratory equipment used to measure the forces between bitumen and probe particles was a Nanoscope AFM (Digital Instrument, Santa Barbra, CA, USA).

A1-2 Bitumen Surface Preparation using a Spin Coating Technique.

The silica wafer was first oxidized in a well-ventilated furnace at 1100 °C for 12 hours to generate a deep blue color. It was then cut into 15x15mm square pieces, was washed with chloroform to remove adsorbed organic contaminants, rinsed with de-ionized water and ethanol, and blow-dried with ultra-pure nitrogen. Bitumen was dissolved in toluene to a concentration of 2.5 mg bitumen per ml toluene. It was centrifuged at 15,000 g-force for 30 minutes to remove all remaining fine solids. About 0.1 ml of the prepared bitumen/toluene solution was dropped slowly onto the silica wafer spinning on the spin coater at 2000 rpm for 20 seconds and 5000 rpm for 1 minute. The bitumen was placed on the substrate in such a manner that the bitumen loss during the coating was minimized. The spin-coated bitumen surface was dried for about one hour in a particle-free horizontal laminar hood under ambient conditions. The thickness of the bitumen layer was estimated to be ca. 100 nm.

A1-3 Probe Particle Preparation

The probe particles tested included single mineral particles of silica and clay, and fines and bitumen from oil sand ores. The particles of silica, clay, and fines were glued with a two-component epoxy onto a tip of short, wide beam AFM cantilever. Spherical silica particles and pseudo-spherical clay particles or fines (agglomerates) of 5~10 μm size were selected under an optical microscope. The glued probe particles were allowed to dry in a vacuum desiccator for more than 24 hours. Prior to each set of experiments, the single mineral probe particles (silica and clays) were thoroughly rinsed with de-ionized water and ethanol, followed by blow-drying with ultra-pure nitrogen. The particles were then exposed to an ultraviolet light for more than 5 hours to remove any possible organic contaminants. The glued fines were used directly for force measurement without further treatment. The particle was then taken out of the solution and allowed to dry for about one hour in a particle-free horizontal laminar hood with the sphere facing up.

A1-4 Colloidal force measurement in a fluid

The AFM consists of a piezoelectric translation stage, a cantilever tip, a laser beam system, a split photodiode and a fluid cell. The working principle of AFM for colloidal force measurement is illustrated in Figure A-1. It is shown that a probe particle is glued on the AFM cantilever tip and the sample is mounted on the AFM translation stage. The particle and substrate are immersed in an aqueous solution of a desired chemistry. A laser beam is focused onto the other side of the cantilever, which is coated with a thin layer of gold to increase the reflectivity of the laser light. The reflected beam is directed by a mirror to a split photodiode, which detects the deflection of the cantilever to a fraction of a nanometer resolution. When the sample on the translation stage moves towards the upper particle under the cantilever, a constant output signal is obtained initially (Figure A-1B: a-b), indicating a zero deflection of the cantilever, i.e., zero force between the two surfaces at large separations. As the lower surface moves further towards the upper particle, either an increase or a decrease in the output signal is seen (Figure A-1B: b-c). An increase in the output signal indicates the cantilever being pushed away while a decrease in the output signal indicates the cantilever being pulled towards the moving surface. The former corresponds to a repulsive force while as the latter reflects an attractive force between the two surfaces in the liquid. Eventually, the lower surface is brought by the translation stage into "contact" with the upper particle. A constant compliance is then observed (Figure A-1B: c-d), indicating that the lower solid surface is pushing the upper particle along with the cantilever upwards. From the known displacement of the piezo translation stage to which the lower surface is attached, the constant compliance allows cantilever displacement (deflection) to be measured in terms of output signals. The cantilever deflection can then be calculated as a function of the separation distance between the two interacting surfaces and the force calculated from the known cantilever spring constant.

At the end of the extension of the piezo translation stage, the piezo starts to retract. If the colloidal force between the two surfaces is purely repulsive, an identical trace of the signal to the approaching branch is likely to be obtained. When there is an adhesion between the two surfaces, the retracting trace follows the dotted line in Figure A-1B. In this case, the cantilever continues to follow the displacement of the piezo translation stage due to the adhesive force holding the particle on the cantilever to the surface on the translation stage. At the point where the restoring force of the cantilever exceeds the adhesive force, a sudden detachment of the particle from the substrate surface occurs, as indicated by the signal returning to zero value. The adhesive force (pull-off force) is calculated from the displacement of the piezo between points R1 and R2 on the retracting branch multiplied by the spring constant of the cantilever. In our experiment, the solution is injected into the fluid cell slowly with great care to avoid trapping air bubbles. Both surfaces immersed in the solution are allowed to equilibrate for 1 hour. To calculate the forces from the measured cantilever deflection, the spring constant of the AFM cantilever is determined by from the measured geometry of the cantilever. For quantitative comparison and theoretical analysis, both the measured interaction force and adhesive force are normalized with the mean radius R of the probe particle.

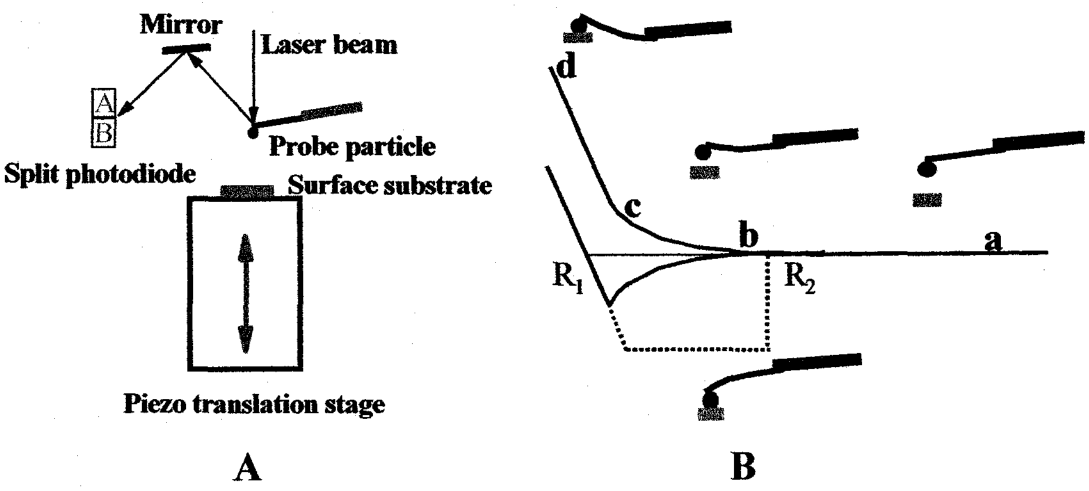


Figure A1-1: Principle of the Atomic Force Microscope.

APPENDEX A2

Table A2-1: Preparation of Solutions of Dissolved Calcium in ppm

Compound	Atomic weight	Times	Total weight
Ca	40.08	1	40.08
Cl	35.453	2	70.906
H	1	12	12
O	15.999	6	95.996
$CaCl_2.6H_2O$			218.982

Concentrations	mg $CaCl_2.6H_2O$/l	mg Ca^{++}/l	ppm Ca^{++}
$CaCl_2.6H_2O$	218.982	40.08	40.08
I ppm Ca^{++}	5.464		

** To prepare 2 liters of solution of dissolved calcium at 40 ppm:

** Add **437.091 mg** $CaCl_2.6H_2O$ into 2 liters water

	Liter of water			
ppm Ca^{++}	1	**2**	3	4
1	5.464	10.927	16.391	21.855
2	10.927	21.855	32.782	43.709
3	16.391	32.782	49.173	65.564
4	21.855	43.709	65.564	87.418
5	27.318	54.636	81.954	109.273
10	54.636	109.273	163.909	218.545
15	81.954	163.909	245.863	327.818
20	109.273	218.545	327.818	437.091
25	136.591	273.182	409.772	546.363
30	163.909	327.818	491.727	655.636
35	191.227	382.454	573.681	764.909
40	218.545	**437.091**	655.636	874.181
45	245.863	491.727	737.590	983.454
50	273.182	546.363	819.545	1092.727
55	300.500	601.000	901.499	1201.999
60	327.818	655.636	983.454	1311.272
65	355.136	710.272	1065.408	1420.545
70	382.454	764.909	1147.363	1529.817

APPENDEX A3

Table A3-1: Preparation of Solutions of Dissolved Magnesium in ppm

Compound	Atomic weight	Times	Total weight
Mg	24.312	1	24.312
Cl	35.453	2	70.906
H	1	12	12
O	15.999	6	95.996
$MgCl_2.6H_2O$			203.214

Concentrations	mg $MgCl_2.6H_2O$/l	mg Mg^{++}/l	ppm Mg^{++}
$MgCl_2.6H_2O$	203.214	24.312	24.312
I ppm Mg^{++}	8.359		

** To prepare 2 liters of solution of dissolved magnesium at 40 ppm:

** Add **668.688 mg** $MgCl_2.6H_2O$ into 2 liters water

	Liter of water			
ppm Mg^{++}	1	**2**	3	4
1	8.359	16.717	25.076	33.434
2	16.717	33.434	50.152	66.869
3	25.076	50.152	75.227	100.303
4	33.434	66.869	100.303	133.738
5	41.793	83.586	125.379	167.172
10	83.586	167.172	250.758	334.344
15	125.379	250.758	376.137	501.516
20	167.172	334.344	501.516	668.688
25	208.965	417.930	626.895	835.860
30	250.758	501.516	752.274	1003.033
35	292.551	585.102	877.654	1170.205
40	334.344	**668.688**	1003.033	1337.377
45	376.137	752.274	1128.412	1504.549
50	417.930	835.860	1253.791	1671.721
55	459.723	919.447	1379.170	1838.893
60	501.516	1003.033	1504.549	2006.065
65	543.309	1086.619	1629.928	2173.237
70	585.102	1170.205	1755.307	2340.409

APPENDEX A4

Published papers:

T. Kasongo, Z. Zhou, Z. Xu and J. Masliyah:" Effect of Clays and Calcium Ions on Bitumen Extraction from Athabasca Oil Sands Using Flotation", The Can. J. Chem. Eng.,Vol. 78, 674-681, August 2000

Effect of Clays and Calcium Ions on Bitumen Extraction from Athabasca Oil Sands Using Flotation

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A novel approach, based on the doping of rich estuarine oil sands with calcium and/or clays, was developed to study bitumen extraction. The batch flotation tests showed that the addition of either calcium ions up to 40 p.p.m., or kaolinite, illite and montmorillonite clays at 1 wt% of oil sands processed had marginal effect on bitumen recovery from the estuarine ores. A sharp reduction in bitumen recovery was observed only when calcium ions greater than 30 p.p.m. and 1 wt% montmorillonite clays were added together. While bitumen recovery correlated well with changes in water/air/bitumen contact angle, no correlation was found between bitumen recovery and measured zeta potential of clays or surface tension of the supernatants from the flotation slurry. The wettability of bitumen was identified as a key element in determining bitumen recovery. The aqueous solution analysis for calcium ions showed that most of the added calcium ions disappeared from the solution when montmorillonite clays were present. The addition of illite or kaolinite clays changed the calcium ion concentration in the slurry only marginally. Stronger adsorption of calcium ions on montmorillonite than on either kaolinite or illite is considered to be responsible for the increased bitumen wettability, and hence reduced bitumen recovery.

Une nouvelle méthode s'appuyant sur le dopage de sables pétrolifères d'estuaires riches avec du calcium et/ou des argiles, a été mise au point pour étudier l'extraction de bitume. Les essais de flottation discontinus montrent que l'ajout soit d'ions de calcium jusqu'à 40 p.p.m., ou d'argiles de kaolinite, illite et montmorillonite à 1% en poids de sables pétrolifères traités a un effet marginal sur la récupération de bitume de gisements estuariens. On a observé une forte réduction de la récupération de bitume seulement lorsque des ions de calcium à une concentration supérieure à 30 p.p.m. et 1% en poids d'argiles de montmorillonite étaient ajoutés ensemble. Tandis que la récupération de bitume montre une bonne corrélation avec les changements d'angle de contact eau/air/bitume, aucune corrélation n'a été trouvée entre la récupération de bitume et le potentiel zéta mesuré des argiles ou la tension de surface des surangeants de la suspension de flottation. La mouillabilité du bitume est apparue comme un élément clé pour déterminer la récupération de bitume. L'analyse de la solution aqueuse pour les ions de calcium montre que la plupart des ions de calcium ajoutés disparaissent de la solution en présence d'argiles de montmorillonite. L'ajout d'argiles d'illite ou de kaolinite ne modifie que marginalement la concentration d'ions de calcium dans la suspension. Une plus forte adsorption des ions de calcium sur la montmorillonite par rapport à la kaolinite ou illite est considérée comme étant responsable de la mouillabilité accrue du bitume, d'où la moins grande récupération de bitume.

Keywords: oil sands, bitumen flotation, oil sands processing, bitumen recovery.

Extraction of bitumen from Athabasca oil sands in Alberta, Canada, represents one of the largest mining operations in the world. More than half million tons of oil sands are processed daily (Hepler and Hsi, 1989; Kasperski, 1992) by Suncor Energy Inc. and Syncrude Canada, Ltd. using the Clark Hot Water Extraction (CHWE) Process (Hepler and Smith, 1994). In this process, mined oil sands are digested and aerated in a tumbler, with a small amount of caustic addition, at a slurry temperature about 75°C to 80°C. The elevated temperature and caustic are used to facilitate bitumen separation (liberation) from sand grains. The conditioned slurries are then fed to a primary separation vessel (PSV). The liberated bitumen droplets, mostly engulfing air bubbles, are floated to the top of the pulp, forming a bitumen-rich primary froth in the PSV. The middlings from the separation vessel are further processed in conventional mechanical flotation cells to recover the remaining bitumen. The tailings from the PSV and the flotation cells contain mainly coarse sands and mineral fines with small amount of fugitive fine bitumen droplets. Approximately one million cubic metres of tailings are discharged into a tailings pond daily.

Handling such a large volume of tailings represents one of the major environmental challenges. In general, fine tailings, after segregation of coarse sands, take several years to consolidate to a solid content of about 30% by weight. The resulting sediment is called mature fine tailings (MFT). Further consolidation of the MFT to a trafficable surface, capable of supporting a productive soil layer would require hundreds of years. Compounded with continuous generation of new tailings, reclamation of tailings ponds becomes a major issue for further oil sands exploration. To reduce the areas for tailings disposal by rapid release of water for recycle to the extraction, a new tailings management scheme, called consolidate or composite tailings (CT) process, was developed at Syncrude Canada Ltd. and Suncor Energy Inc. In this new process, the addition of coarse sands and about 1 kg/m^3 of gypsum to the MFT accelerated consolidation of the MFT to a solid content as high as 82% by weight within 30 days. The adoption of the process can potentially result in a bitumen extraction operation at near-zero waste discharge.

However, the use of gypsum in the CT process is anticipated to increase the concentration of calcium and other associated ions in the recycle water to bitumen extraction. The negative impact of these ions on oil sands processability has been observed in both commercial operations and extensive laboratory tests using batch extraction unit (BEU) (Sanford and Seyer, 1979; Sanford, 1983; Smith and Schramm, 1992). Unfortunately, the exact reason(s) for such negative effect remains to be further explored. Lack of sensitive techniques and systematic studies, compounded with the complex nature of oil sands and their extraction systems, appears to be responsible for slow progress in this area.

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A few conceptual models incorporating calcium ions and various related components were proposed to explain some observations in bitumen extraction (Bowman, 1967; Takamura and Chow, 1983; Takamura and Wallace, 1988; Sengupta and Tollefson, 1997; Zhou et al., 1999). Bowman (1967) and Takamura and Chow (1983) adopted the electrical double-layer theory to explain the observed bitumen depression by considering the effect of calcium ions on bitumen–sands interactions. Sengupta and Tollefson (1997), on the other hand, suggested that the formation of calcium carboxylic complexes played a role in bringing bitumen/solids and solids/air bubbles together, thereby retarding bitumen recovery and affecting bitumen froth quality. More recently, Zhou et al. (1999) proposed that the interaction of bitumen with silica in the presence of calcium ions would be mainly due to the hydrophobic interaction. Using a surfactant free-model oil system, they demonstrated that calcium ions present in the bulk solution or within the electrical double layer of the silica and oil droplets do not enhance the coagulation of fine silica with the oil droplets. In the case of diluted bitumen, the calcium ions adsorbed on silica interact with carboxylic groups either in solution or on bitumen surfaces. As a result, silica becomes hydrophobized and hence coagulates with bitumen via hydrophobic interaction. To predict the impact of the recycle water from the CT process on bitumen recovery, it is necessary to understand the role of various species in different stages of the bitumen flotation process. This communication discusses the effect of different types of clays and calcium ions, alone or in combination, on bitumen recovery using flotation. The results obtained allow us to substantiate the applicability of our model (Zhou et al., 1999) to the explanation of the observed effect of calcium ions and clays on bitumen flotation.

Experimental

Methodology and Materials

The effect of calcium ions and fine solids on depressing bitumen flotation has been demonstrated previously, using oil sands samples mixed with process water (Hepler and Hsi, 1989; Hepler and Smith, 1994). Since both calcium ions (and other multi-valent metal ions) and fine clays were present in the slurry, it was difficult to distinguish whether the depressed effect was due to the fine clays or calcium alone, or the combination of the two. To identify the role of each individual parameter in bitumen extraction, it is necessary to isolate the interactions among different variables. For this purpose, a novel approach was devised in our study by doping a model oil sands sample containing minimal amount of fine clays and calcium content. With this approach, the effect of calcium and fine clays, one or in combination, on bitumen extraction can be investigated.

Based on this methodology, estuarine ores containing about 10.8% bitumen, referred to as high grade ores from Syncrude Canada, Ltd., were used as a model oil sands sample in this study. The bulk ore sample was homogenized, packed in plastic bags and stored in a deep freezer at –29°C to minimize oxidation. The atomic absorption (AA) analysis of the solution from the conditioned oil sands slurry showed a calcium concentration of 0.5 p.p.m. (Table 1), confirming that the original oil sands sample contained a negligible amount of soluble calcium ions. Three different types of clay powders, kaolinite, illite and montmorillonite were purchased from Wards Minerals and used as received. The clay samples showed the release of undetectable amount of soluble calcium ions, suitable for the current study.

Table 1. Measured residual calcium concentration in tailings water of bitumen extraction from high grade oil sands.

	No Ca^{++} addition	Ca^{++} Addition (40 p.p.m.)
	Residual Ca^{++} (p.p.m.)	Residual Ca^{++} (p.p.m.)
No clay addition	0.5	27.4
Montmorillorite	0.1	3.0
Illite	0.5	21.4
Kaolinite	0.3	21.0

The Reagent grade of $CaCl_2 \cdot 6H_2O$ (BDH) was used as received. Unless otherwise stated, all the experiments were conducted in de-ionized water with a resistivity of 18.2 MΩ cm, produced using an Elix-5 (Millipore, Canada). The reason for using de-ionized water, rather than process water from the tailings pond, is to avoid the complication of the existing chemical species (including calcium ions) in the process water in interpreting the results.

Testing Procedures

Bitumen Flotation

Although the standard BEU tests (Sanford and Seyer, 1979) have been extensively used to evaluate bitumen processability in the oil sands industry, only the overall bitumen recovery is accessible from these tests. To obtain the information on bitumen flotation kinetics, a modified laboratory Denver flotation cell, one litre in capacity, was used in bitumen flotation tests. To control the temperature of flotation, a water jacket connected to a thermal bath was attached to the Denver cell. While the slurry density, temperature, conditioning time and aeration rate were kept the same as used in the typical BEU tests (Sanford and Seyer, 1979), the primary bitumen froth was collected as a function of time to obtain the kinetic information of bitumen flotation. For each test, 450 g of oil sands were dispersed in 300 mL of de-ionized water at 80°C under mechanical agitation of 1800 r.p.m. The air flowrate during this period was controlled at 150 mL/min. After slurry was conditioned for 5 min, 650 mL of flood water at 80°C was added into the slurry without aeration. Bitumen froth was then collected as a function of time for a period of 10 min. The aeration was restarted at an airflow rate of 50 mL/min to collect the *secondary* froth product for an additional 5 min. The representative feed samples and all the products, including tailings slurry remained in the cell, were preserved for bitumen assays. This procedure allows bitumen recovery as a function of flotation time and flotation rate constant to be evaluated. The measured pH of the tailings water for all the tests was in the range of 7.5 to 8.0.

Bitumen Assays

The amount of bitumen in various product streams was determined using similar procedures described by Dai and Chung (1996). To confirm the accuracy of the assay method, a set of tests was conducted by dissolving a given amount of coker feed bitumen into a known volume of toluene. The resultant solution was mixed with water in a sealed bottle and shaken for 30 min on a mechanical shaker (Fisher). The mixture was left overnight to ensure complete dissolution of bitumen in toluene. About 30 mL of the resultant suspension was then transferred to a centrifuge tube and centrifuged at 35 000 g for 20 min to ensure a complete phase separation. About 5 to 10 mL of organic phase (i.e., diluted bitumen) at the upper portion of the tube was transferred to a glass vessel and weighed accurately. The sample was kept in a vacuum oven at 50°C to evaporate the toluene. The weight change of the sample with time was recorded, and a relatively constant weight was achieved after a 48-h period of drying. This weight was regarded as the weight of bitumen sampled. Within the experimental error, the agreement between the measured and prepared bitumen/toluene ratios was found to be satisfactory, with an optimal bitumen to toluene ratio of 0.12 to 0.25.

Zeta Potential Measurement

The electrokinetics of different clays was examined using a Lazer-Zee meter (Model 501, Penkem). Fine clay suspensions of 0.1 wt% solids were prepared in 1 mM supporting electrolyte (KCl) solutions. After conditioning the suspension with or without added calcium ions for 10 min, about 35 mL of suspension was transferred to an electrophoresis cell with the help of a laboratory syringe. The zeta potential was read directly from the meter at an apparent zero net particle movement under the eyepiece. Zeta potential values reported in this study are the average of three independent readings.

Contact Angle Measurement

To assess bitumen surface hydrophobicity in a bitumen flotation system, contact angles were measured using a captive bubble method (Zhou et al., 1998). A layer of coker feed bitumen (supplied by Syncrude Canada Ltd.) was spread on a methylated glass slide and heated to 80°C briefly. After cooling down the slide, the resultant bitumen surface can be considered molecularly smooth due to the action of surface tension force. To simulate bitumen-clay interactions in a batch bitumen extraction process, the coker feed bitumen-coated slide was immersed in an aqueous suspension containing 0.5 wt% clay with or without added calcium ions. The suspension in the beaker was kept at about 80°C and stirred with a magnetic stirrer for 20 min, The bitumen coated glass slide was then transferred to a square glass vessel (3 x 3 cm) containing de-ionized water as probing liquid. An air bubble was subsequently generated at the tip of a micro-syringe and made in contact with the bitumen layer. The contact angle was measured through the water phase using a goniometer (Rame Hart). The water receding contact angles were recorded in this study because it is more akin to bitumen–bubble attachment in a flotation process. The contact angle was read from both sides of the bubble as quickly as bubble–bitumen attachment was made to avoid the possible spreading (engulfing) of bitumen on the bubble. The values reported in this communication are the average of five independent measurements. To investigate the strength of bitumen–air bubble attachment, photographs were taken for a bubble to approach to, and retract from a layer of bitumen froth obtained right after bitumen flotation.

Water Analysis

The tailings water samples taken at the end of a flotation test were centrifuged at 35 000 g for 20 min. The supernatants obtained were used for calcium ion analysis and surface tension measurement. Calcium ion concentration of flotation tailings water was determined using an atomic absorption spectrometer. With the atomic absorption, a detection limit of 0.3 p.p.m. calcium was achieved. The surface tension of the tailings water, on the other hand, was determined using a plate method with an automated process tensiometer (K-12, Kruss, USA). Three independent measurements were performed and the average was reported. Between each measurement, the plate was flame cleaned after rinsing with ethanol. With this instrument, the surface tension of de-ionized water used in this study can be measured to an accuracy of 71.7 ± 0.2 mN/m at room temperature.

Results

Effect of Calcium Ions and Clays

To understand the role of CT water chemistry in bitumen extraction, the effect of metal ions and different type of clays (kaolinite, illite and montmorillonite) on bitumen extraction needs to be examined individually and collectively as desired. For this purpose, processability of high grade oil sands ore is used as the baseline for comparison. A set of repeating baseline tests was conducted and the results in Figure 1 show a satisfactory repeatability, demonstrating that the use of the modified Denver cell can effectively evaluate bitumen flotation performance. Also shown in Figure 1 is a fast flotation kinetics of high grade oil sands under natural flotation conditions, with about 90% bitumen being floated within 2 min. By assuming a first order rate process for the batch flotation (Agar et al., 1980; Xu et al., 1996), a flotation rate constant of 1.1 min^{-1} (Table 2) was obtained. Although an estimate of the bitumen recovery at the early stage was not accessible, our results here represent the first attempt in collecting data of bitumen flotation kinetics.

To examine the effect of calcium ions on bitumen flotation, a given amount of calcium ions was added to the oil sands slurry during conditioning. The flotation results were compared with those from the baseline tests. It is clear that any changes in bitumen recovery would be attributed to the effect of added calcium ions. Based on the reported calcium ion concentration

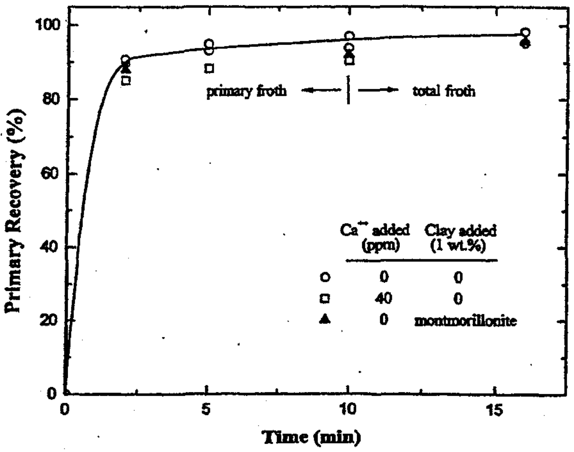

Figure 1. Effect of calcium ions and clay on bitumen flotation kinetics (high grade oil sands, flotation at 80°C).

Table 2. Estimation of flotation rate constant *K* (in the presence of 1 wt% montmorillonite).

$$R = R_{\infty} [1 - e^{-K}(t + \tau)]$$

R: recovery at time *t*, (%); R_{∞}: recovery at time infinite, (%); *K*: flotation rate constant, (min^{-1}); *t*: flotation time, min.; τ: zero time correction factor, min.

Calcium addition (p.p.m.)	R_{∞} (%)	*K* (min^{-1})	τ (min)
0	95.7	1.1	0.5
10	95.3	0.8	0.5
30	88.8	0.7	0.5
35	85.0	0.6	0.5
40	73.3	0.4	0.5

in the recycle water from the tailings pond being typically less than 40 p.p.m., the addition of calcium ions up to 40 p.p.m. was examined. The flotation results given in Figure 1 showed a moderate depression in primary bitumen recovery from 96% to ca. 90%. Considering experimental error involved in these tests, our results appear to show that calcium alone up to 40 p.p.m. may not be a major concern for processing estuarine ores. This observation appears to be inconsistent with the calcium effect reported previously with reference to bitumen extraction using process water. The reason for this discrepancy may be attributed to the presence of other ionic species in the process water, compounded with the complex nature of oil sands ore. This effect is illustrated later in our doping tests.

The effect of individual clays alone on bitumen recovery was also examined. The oil sands slurry was prepared in kaolinite, illite or montmorillonite suspensions at 1 wt% of the oil sands sample. The results in Figure 1 show that without the addition of calcium, introducing montmorillonite clays did not impose any significant impact on bitumen recovery. The similar observation was made for kaolinite and illite clays. This finding suggests that the presence of fine clays alone up to 1% weight of the oil sands should not be a concern for bitumen recovery if the estuarine ores are processed using fresh water of low concentration metal ion species. It should be noted that the change of bitumen content in the feed due to clay addition is considered negligible.

As fine clays and calcium ions are present in oil sands (especially in marine ores) and recycle water, the undesired synergistic effect of the two is considered and simulated in the following tests. The bitumen flotation was conducted, in this case, with the addition of calcium ions and clays in the oil sands slurry. The results in Figure 2 show that increasing calcium ion concentration up to 40 p.p.m., together with the addition of illite or kaolinite clays, did not interfere with the bitumen flotation substantially. However, the addition of 1 wt% montmorillonite clays caused a sharp reduction in bitumen recovery at calcium ion concentrations above 30 p.p.m. The addition of 40 p.p.m. calcium ions, for example, decreased the primary bitumen recovery from 93% to less than 70%. Accompanied was a significant decrease in flotation rate constant from 1.1 min^{-1} to 0.4 min^{-1} as shown in Table 2. It can be argued that the flotation rate constant is dependent on hydrodynamics of a flotation system. Under a fixed hydrodynamic condition as in the present case, the observed variation in flotation rate constant cannot be attributed to hydrodynamic effects, but rather related to the changes in the system chemistry. The results in Figure 2 appeared to suggest that calcium ions triggered the interactions between montmorillonite clays and bitumen, probably by slime-coating of montmorillonite on the bitumen surface.

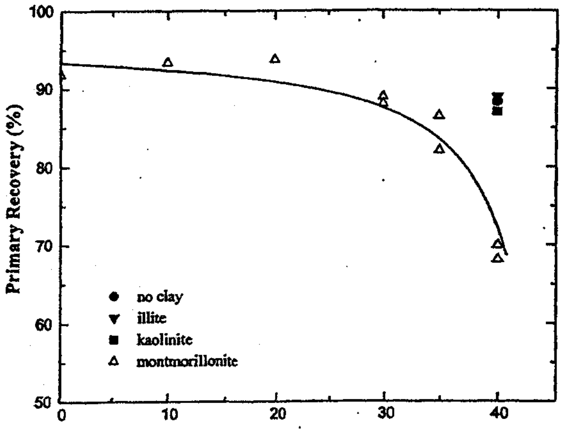

Figure 2. Synergistic effect of calcium ions and clays on bitumen flotation recovery (high grade oil sands, flotation at 80°C).

Effect of Surface Properties of Clays and Bitumen

One of the consequences of the presence of clays and/or other fine minerals in a flotation process is the potential slime coating, i.e., the fine solids become coated on a targeted particle. The coating of hydrophilic clays on a naturally hydrophobic bitumen droplet inevitably depresses bitumen flotation by setting up a barrier for bubble–bitumen attachment. Slime-coating also deteriorates the quality of bitumen froth by carrying undesired solids to the froth product. To search for the explanations as to why bitumen flotation responded differently to different types of clays added, zeta potentials of clays and water/air/bitumen contact angles were measured.

Zeta Potential

The measured zeta potentials of three different types of clay samples are presented in Figure 3. Figure 3a shows that in the absence of calcium ions, all the clays tested carry a net negative surface charge in the aqueous solutions over a pH range from 3 to 12. The main difference among the three clays is that the zeta potential of kaolinite clays is less negative. With the addition of 40 p.p.m. calcium ions (Figure 3b), the absolute values of zeta potential decreased for all the clays, as anticipated. At pH 7.5 to 8.0, where the flotation was conducted, similar zeta potentials were obtained for kaolinite and montmorillonite, higher than that for illite clays over this pH range. Since the electronkinetics of koalinite and montmorillonite in the presence of calcium ions are similar while the drastically different impact of these clays on bitumen recovery was observed (Figures 1 and 2), it is evident there was no correlation between the measured zeta potentials and the observed flotation perfor-

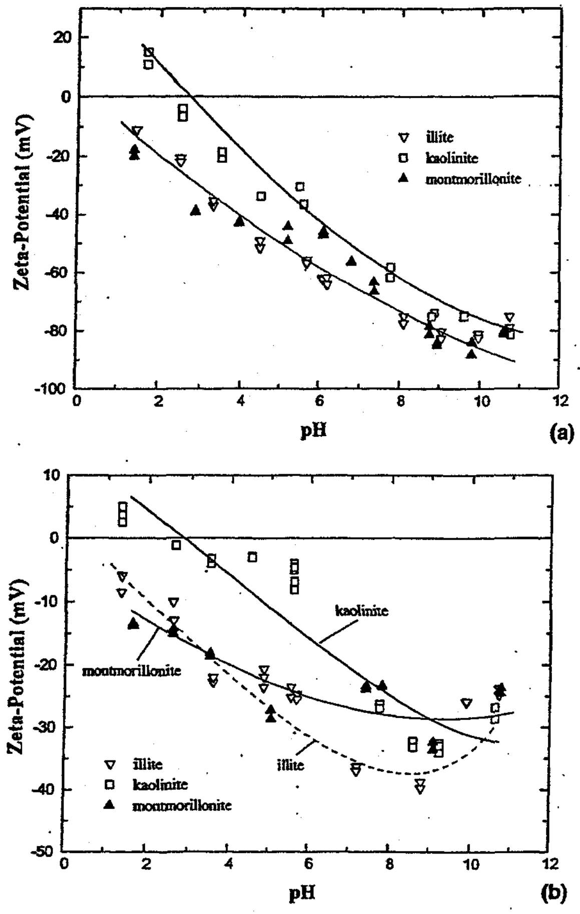

Figure 3. Zeta potentials of clays in aqueous solutions (10^{-3} M KCl): 3(a) without calcium ions addition; 3(b) 40 p.p.m. calcium ions added.

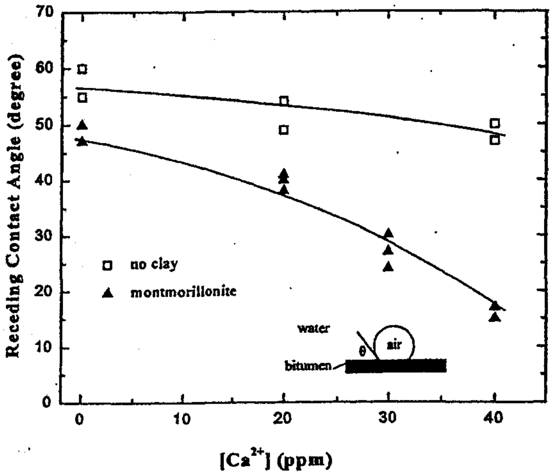

Figure 4. Receding contact angle of water on a coker feed bitumen layer conditioned in aqueous suspensions.

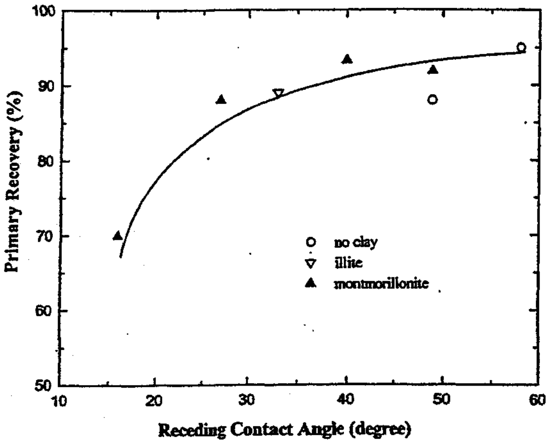

Figure 5. Correlation between bitumen recovery and receding contact angle of water on bitumen.

mance. The measured zeta potential values for three clays alone can not account for the observed depression of bitumen flotation by calcium ions in combination with montmorillonite clays, but not with kaolinite or illite clays.

Water Receding Contact Angle

Flotation is a surface wettability-based separation technique. The measured contact angle in bitumen–air–water system would serve as a marker to indicate how the water chemistry affects the hydrophobicity and hence floatability of bitumen. In this study, the water receding contact angles were recorded and the results are shown in Figure 4. For bitumen immersed in de-ionized water, a receding contact angle of about 60° was obtained, confirming that bitumen is naturally hydrophobic. By conditioning bitumen in 40 p.p.m. calcium ion solutions, the receding contact angle decreased gradually from about 60° to 50°. This is a strong indication of the interactions between calcium ions and bitumen surfaces, probably by the formation of calcium carboxylic complexes on the bitumen surfaces. The reduced contact angle accounts for a marginal reduction in primary bitumen recovery (see Figure 1). When conditioned with 0.5% montmorillonite suspensions, a reduction in receding contact angle from about 60° to 50° was observed. Again, this reduction corresponded well with a marginal reduction in bitumen recovery. A drastic change in receding contact angle from ca. 50° to less than 20° was observed when bitumen layer was conditioned in 0.5 wt% montmorillonite suspensions containing 40 p.p.m. calcium ions. Such a reduction in receding contact angle would suggest the modification of bitumen surface by either adsorbed calcium ions or coated clays on bitumen surfaces. This observation confirms the adverse synergetic action of calcium ions and montmorillonite in bitumen extraction: retarding bitumen/air bubble attachment and contributing to a reduced bitumen recovery as seen in Figure 2.

To establish whether there is a correlation between bitumen recovery and receding contact angle, the primary bitumen recovery is plotted against the measured receding contact angles in Figure 5. A general correlation appears to exist between primary bitumen recovery and the receding contact angle. A higher bitumen recovery is associated with a greater contact angle. Falling below a critical receding contact angle value around 30° tends to indicate a significant drop in bitumen recovery. The convex shape of the curve in Figure 5 also suggests that the contact angle is a more sensitive marker than flotation recovery to indicate the changes in bitumen extraction conditions. For example, a double in contact angle corresponded to a change in recovery by only about 30%.

Bitumen–Bubble Attachment

In an attempt to visualize how the water chemistry affects the fundamental process of bitumen flotation, the effect of bitumen surface wettability on bitumen flotation was further demonstrated in a simple air bubble–bitumen attachment/detachment test. After collecting bitumen froth from bitumen flotation on a piece of methylated glass slide, the attachment between an air bubble and the bitumen froth was made in de-ionized water. The attachment process was directly viewed on a monitor connected to a CCD-VCR system, and the images were recorded. Because of the obvious roughness of the bitumen froth layer, as observed from the images (Figure 6), no attempt was made to obtain the contact angle values in this case. Instead, the strength of the attachment was assessed qualitatively by visualizing images shown in Figure 6. The images taken with high grade oil sands under natural flotation conditions (Figure 6a) showed a strong bubble–bitumen attachment as the bubble changed from convex (B) to concave (C) shape during bubble retracting. In fact, the attachment was so strong that the bitumen–air bubble contact did not break. Instead, the bubble itself breaks, leaving part of the bubble on the bitumen (D). Such a strong attachment would translate to a high bitumen recovery as the bitumen detachment from air bubble would be negligible. In contrast as shown in Figure 6b, the bubble deformed only to a plenary shape (C) before it detached from the bitumen floated with the addition of 40 p.p.m. calcium ions and 1 wt% montmorillonite. The bitumen layer was not affected, as shown by the image D of Figure 6b. Clearly, the weaker adhesion is a manifestation for the observed sharp decrease in bitumen recovery by combined action of calcium ions and montmorillonite. It is possible that the hydrodynamic forces during flotation may detach the bitumen from air bubbles due to the weak adhesion force holding them together, contributing to the reduced bitumen recovery. The similar observation was made for bitumen froth obtained from a low grade oil sands ore under natural flotation conditions. This may suggest that adding 40 p.p.m. calcium ions and 1 wt% montmorillonite caused high grade oil sands to behave similar to low grade oil sands, resulting in a low primary bitumen recovery.

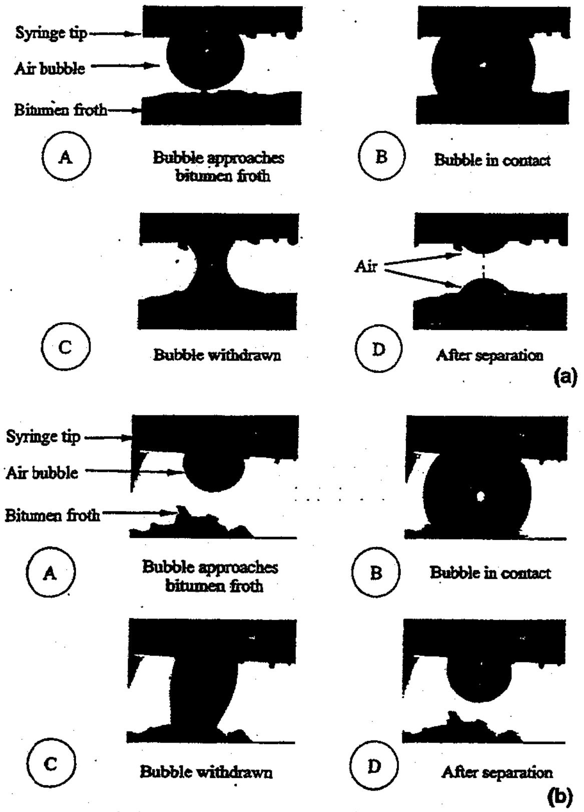

Figure 6. Visual observation of bitumen–air bubble attachment strength: (a) bitumen froth from high grade oil sands floated under natural conditions; (b) bitumen froth from high grade oil sands floated with 40 p.p.m. calcium ions and 1 wt% montmorillonite being added.

Process Water Analysis

To examine the possible changes in aqueous phases when calcium ions and/or clays were added to oil sands slurry, the residual calcium ions remained in flotation tailings water samples were determined. Without calcium ion addition, calcium ions released from the high grade oil sands ore sample are only 0.5 p.p.m., in the range of the accurate detection limit (Table 1). In contrast, a level of 12 p.p.m. calcium ions was detected in the tailings water samples from the low grade oil sands slurry. Table 1 also shows that adding clays alone to the high grade oil sands slurry did not change the residual calcium ion concentration (0.1 to 0.5 p.p.m.), suggesting that no additional calcium ions were released from the added clays. In the absence of clays, the addition of 40 p.p.m. calcium ions to the high grade oil sands slurry resulted in a residual calcium ion concentration about 27.4 p.p.m. in the tailings water. This may suggest the uptake of 12.6 p.p.m. calcium ions on solids and/or bitumen, corresponding to 0.027 mg calcium per gram of oil sands. The calcium uptake by oil sands at this level caused a marginal reduction in primary bitumen recovery (Figure 1). It is interesting to note that with the addition of 40 p.p.m. calcium ions and 1 wt% illite and kaolinite clays to the high grade oil sands slurry, about 21 p.p.m. calcium ions were detected in the tailings water. This finding suggests a minimal synergetic effect of calcium with illite or kaolinite on bitumen recovery as observed. When 1 wt% montmorillonite and 40 p.p.m. calcium ions were added, however, only 3 p.p.m. calcium ions were detected in the high grade oil sands slurry. Since we have established that the addition of montmorillonite did not release additional calcium ions into the slurry, the further reduction of soluble calcium ions to 3 p.p.m. upon montmorillonite addition accounts for 4.6 mg calcium uptake per gram of clays. The substantial uptake of calcium by montmorillite clays appears to be the cause for the observed reduction of receding contact angle (Figure 4), and depression of bitumen recovery (Figure 2).

Table 3. Measured surface tension of tailings water from bitumen extraction of high grade oil sands.

	No Ca^{++} addition (mN/m)		Ca^{++} Addition (40 p.p.m.) (mN/m)	
No clay addition	58.6	95.9%	57.2	58.2%
Montmorillonite	57.9		59.9	48.1%
Illite	57.9		59.2	38.8%
Kaolinite	57.8		59.2	86.9%
De-ionized water	71.7		70.6	

The surface tension of the tailings water (Table 3) was found to be significantly lower than that of de-ionized water, suggesting the release of surface-active species from bitumen during oil sands conditioning. This finding is consistent with the previous investigations (Bowman, 1967; Moschopedis et al., 1977; Ali, 1978; Sanford and Seyer, 1979; Schramm and Smith, 1987) in which two classes of anionic surfactants (i.e., carboxylates and sulphonates/sulphates) were reported to be released from bitumen into the oil sands slurry. It is interesting to note that the surface tension of the tailings water did not change substantially with the addition of calcium and clays to high grade oil sands slurry. These findings suggest that the surface tension may not be a key parameter in determining bitumen floatability from the oil sands examined in this study. The on-line visualization in our group (Zhou et al., 2000) confirmed the generation of abundant fine bubbles in the process water from both high grade and low grade oil sands slurries, supporting the results of surface tension measurements.

Discussion

The poisoning of a model high grade oil sands ore by calcium ions and clays employed in this study allowed the identification of the major factors affecting bitumen recovery. This novel approach has furthered our understanding of the role of water chemistry in bitumen flotation. From modified Denver flotation tests, the detrimental role of calcium ions in combination with montmorillonite has been identified. In conjunction with solution analysis, the negative impact of calcium ions and montmorillonite on bitumen flotation recovery has been found to be associated with the uptake of more calcium ions by montmorillonite clays than by kaolinite or illite clays. One possible reason for this phenomenon may be due to a much larger specific surface area and stronger cation exchange capacity for montmorillonite than for kaolinite or illite (van Olphen, 1977). The calcium ions uptaken by montmorillonite activated the interactions between montmorillonite and bitumen, resulting in a reduced bitumen hydrophobicity. Consequently, the bitumen–bubble attachment was weakened, as demonstrated in Figure 6. While zeta potentials of the three different clays tested did not show any correlation with the bitumen recovery (Figures 2 and 3), a qualitative correlation between bitumen recovery and receding contact angle was established (Figure 5).

The results obtained from this study suggest that the effect of calcium ions on bitumen–clay interaction was dependent on the type of clays present. As shown in Table 1, only a small portion of calcium ions was uptaken by kaolinite or illite clays. It is clear that calcium ions in the solution or accumulated in the electrical double layers of kaolinite and illite clays would not induce the interactions between clay and bitumen, and therefore their presence has a minimal effect on bitumen recovery. This is in line with our previous observations that in the absence of surfactant, calcium ions did not induce the coagulation of hydrophilic silica with hydrophobic oil droplets, unless the silica was made hydrophobic (Zhou et al., 1999). It is important to note that bitumen flotation is a far more complex system than what we have just discussed. The water chemistry would affect all the interactions among all the phases involved, including clay–clay, clay–air, air–air, air–bitumen, bitumen–clay and bitumen–bitumen, etc.. Should the added calcium predominately affect the air bubbles (just like surfactants), its effect on the overall bitumen recovery would be negligible. This is because calcium ions will be quickly removed from the system by ion flotation (Sebba, 1962) at the early stage of flotation tests. Clearly, the interaction of calcium with clays is a key parameter in the present case. In addition, with the added calcium up to 40 p.p.m. without clay addition, only a minimal effect on bitumen flotation was observed. The results further illustrate that the interaction of calcium with air bubbles is not the major player.

To account for the observed adverse synergy of calcium and montmorillonite on bitumen flotation, strong affinity of calcium with montmorillonite appears to be the key element. The adsorbed calcium ions on montmorillonite clays would interact with carboxylic groups of natural surfactant on bitumen droplets or released into solution to form insoluble calcium carboxylate. The former scenario appears to be more likely the case as the coated clays may remain hydrophilic, thereby reducing bitumen–bitumen coalescence and air bubble–bitumen attachment with clays as steric barrier. This scenario is consistent with the observed reduction in contact angle after bitumen being conditioned in montmorillonite suspensions containing 40 p.p.m. calcium ions (Figure 4). Should the latter be the case, the clays may become moderately hydrophobized. The modification of clays from hydrophilic to hydrophobic during oil sands processing is well documented (Ignasiak et al., 1985; Kotlyar et al., 1985; McIntyre et al., 1986). The coating of hydrophobic clays on bitumen and/or bubble surface via hydrophobic interaction is therefore anticipated, contributing to a poor bitumen froth quality. Our results are consistent with the experienced poor processability of marine ores which are characterized by a high fines content and calcium (or other multivalent metal ions) release. It is clear that knowing the amount and distribution of calcium (or other multivalent metal ions) in the system helps in diagnosing the problems encountered in oil sands processing.

In the literature, the controversy regarding the effect of calcium ions is well documented. Both favourable and unfavourable effects have been reported. It is interesting to note that the results from our controlled tests can be used to account for some inconsistencies of the existing observations from various laboratories. Taking Figure 2 as an example, the adverse effect of increasing calcium ion concentration would not be observed if oil sands with low fine contents were used in the tests. Translating this knowledge to industrial operations, it is anticipated that CT water would have minimal effect on bitumen extraction from estuarine ores containing low fines content and low concentration of undesirable species, such as calcium and magnesium. This probably is the reason why the commercial extraction process can, sometimes, tolerate a relatively high calcium ion concentration when the ore body contains less amount of fines. Clearly, the observed depression of bitumen recovery in industrial operations by the increased calcium ions in process water can be partially explained by the presence of relatively large amount of fines in feed ores.

Conclusions

A novel approach was developed based on the doping of model oil sands sample with calcium and/or clays. This approach allows the effect of water chemistry and ore characteristics on bitumen extraction to be examined. The use of a modified Denver flotation cell allowed bitumen flotation kinetics to be examined for the first time. The following conclusions can be drawn based on our experimental results:

1. The presence of calcium ions up to 40 p.p.m. Ca^{2+} or kaolinite, illite and montmorillonite clays alone at 1 wt% of oil sands processed had marginal effect on bitumen flotation of high grade oil sands ore. A sharp reduction in bitumen flotation rate constant and overall bitumen recovery was observed only when both calcium ions and montmorillonite clays were added together.
2. Solution analysis revealed that the adverse impact of calcium ions and montmorillonite clays on bitumen flotation kinetics was associated with stronger affinity of calcium on montmorillonite clays than on kaolinite or illite clays.
3. The calcium ions uptaken by the montmorillonite clays mainly interact with carboxylic groups on bitumen droplets to form insoluble calcium carboxylate, triggering clay deposition on bitumen and reducing the contact angle of water on bitumen.
4. A qualitative correlation between bitumen recovery and contact angle is established. Neither zeta potentials of clays nor surface tension of the supernatants from flotation tailings slurry appears to correlate with bitumen recovery. The observations in this study suggest that the variation in bitumen wettability with water chemistry is a key element in determining bitumen floatability.

Acknowledgements

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References

Agar, G.E., R. Stratton-Crawley and T.J. Bruce, "Optimizing the Design of Flotation Circuit", CIM Bulletin 73, 173–181 (1980).

Ali, L.H., "Surface-Active Agents in the Aqueous Phase of the Hot-Water Flotation Process for Oil Sands", Fuel 57, 357–367 (1978).

Baptista, M.V. and C.W. Bowman, "The Flotation Mechanism of Solids from the Athabasca Oil Sands", Preprint, 19th Can. Chem. Eng. Conf., Edmonton, AB (1969).

Bowman, C.W., "Molecular and Interfacial Properties of Athabasca Tar Sands", Proc. 7th World Petrol. Congr. 3, 583–604 (1967).

Dai, Q. and K. Chung, "Hot Water Extraction Process Mechanism Using Model Oil Sands", Fuel 75, 220–226 (1996).

Hepler, L.G. and R.G. Smith, "The Alberta Oil Sands: Industrial Procedures for Extraction and Some Recent Fundamental Research", AOSTRA Technical Publication Series #14, Alberta Oil Sands Technology and Research Authority, Edmonton, AB (1994).

Hepler, L.G. and C. Hsi, "AOSTRA Technical Handbook on Oil Sands, Bitumens and Heavy Oils", AOSTRA Technical Publication Series #6, Alberta Oil Sands Technology and Research Authority, Edmonton, AB (1989).

Ignasiak, T.M., Q. Zhang, B. Kratochvil, C. Maitra, D.S. Montgomery and O.P. Strausz, "Chemical and Mineral Characterization of the Bitumen-Free Athabasca Oil Sands Related to the Bitumen Concentration in the Sand Tailings from the Syncrude Batch Extraction Test", AOSTRA J. Research 2, 21–35 (1985).

Kasperski, K.L., "A Review of Properties and Treatment of Oil Sands Tailings", AOSTRA J. Research 8, 11–15 (1992).

Kotlyar, L.S., B.D. Sparks and H. Kodama, "Some Chemical and Mineralogical Properties of Fine Solids Derived from Oil Sands", AOSTRA J. Research 1, 99–106 (1985).

McIntyre, D.D., D.S. Montgoemry and O.P. Strausz, "Caboxylic Acids Bound to the Mineral Matter in Heavy Cretaceous Oils of Alberta", AOSTRA J. Research 2, 223–231 (1986).

Moschopedis, S.E., J.F. Fryer and J.G. Speight, "Water-Soluble Constituents of Athabasca Bitumen", Fuel 56, 109–110 (1977).

Sanford, E.C., "Processibility of Athabasca Oil Sand: Interrelationship between Oil Sand Fine Solids, Process Aids, Mechanical Energy and Oil Age after Mining", Can. J. Chem. Eng. 61, 554–567 (1983).

Sanford, E.C. and F.A. Seyer, "Processibility of Athabasca Tar Sand Using a Batch Extraction Unit: The Role of NaOH", CIM Bulletin 72, 164–169 (March 1979).

Schramm, L.L., R.G. Smith and J.A. Stone, "The Influence of Natural Surfactants Concentration on the Hot Water Process for Recovering Bitumen from Athabasca Oil Sands", AOSTRA J. Research 1, 5–13 (1984).

Schramm, L.L. and R.G. Smith, "The Influence of Natural Surfactants on Interfacial Charges in the Hot-Water Process for Recovering Bitumen from the Athabasca Oil Sands", Colloids and Surfaces 14, 67–85 (1985).

Schramm, L.L. and R.G. Smith, "Two Classes of Anionic Surfactants and Their Significance in Hot Water Processing of Oil Sands", Can. J. Chem. Eng. 65, 799–811 (1987).

Sebba, F., "Ion Flotation", Elsevier Pub. Co., Amsterdam, The Netherlands (1962).

Sengupta, S. and E. Tollefson, "Recovery, Characterization and Conceptual Modelling of Non-Bituminous Organic Materials from Oil Sands", Can. J. Chem. Eng. 75, 379–390 (1997).

Smith, R.G. and L.L. Schramm, "The Influence of Mineral Components on the Generation of Natural Surfactants from Athabasca Oil Sands in the Alkaline Hot Water Process", Fuel Pro. Tech. 30, 1–14 (1992).

Takamura, K. and R.S. Chow, "A Mechanism for Initiation of Bitumen Displacement from Oil Sands", Can. J. Petrol. Tech. 22, 22–30 (1983).

Takamura, K. and D. Wallace, "The Physical Chemistry of the Hot Water Process", Can. J. Pet. Tech. 27, 98–105 (1988).

van Olphen, H. "An Introduction to Clay Colloid Chemistry", John Wiley & Sons, New York, NY (1977).

Xu, M., P. Quinn and R. Stratton-Crawley, "A Feed-Line Aerated Flotation Column, Part 2: Modelling and Scale-up", Minerals Engineering 9, 655–666 (1996).

Zhou, Z.A., Z. Xu, J.H. Masliyah and J. Czarnecki, "Coagulation of Bitumen with Fine Silica in Model Systems", Colloid and Surfaces 148, 199–211 (1999).

Zhou, Z.A., H. Hussein, Z. Xu, J. Czarnecki and J.H. Masliyah, "Interaction of Ionic Species and Fine Solids with a Low Energy Hydrophobic Surface from Contact Angle Measurement", J. Colloid. Interface Sci. 204, 342–349 (1998).

Zhou, Z.A., Z. Xu, J. Masliyah, T. Kasongo, D. Christendat, K. Hyland, T. Kizior and D. Cox, "Application of On-Line Visualization to Flotation Systems", Proceedings, 32nd Canadian Annual Meeting of Mineral Processors, Ottawa, ON (2000).

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APPENDEX A5

5.1 "Interaction between Bitumen and Additives Interpreted by Zeta Potential Measurement ", Citation from published paper by Liu, J and Xu. Z. (2001)

- Figures 5-9a, 5-10a and 5-11a show Zeta potentials in cases of binary bitumen-clay mixtures. Individual distributions of zeta potentials are centered in ς_B for bitumen and in ς_C for clay particles.

- Figures 5-9b, 5-10b, and 5-11b show the result of mixing bitumen droplets and clay of the 1:1 mass ratio for the case without calcium ion addition. There are still 2 distinct picks with a slight shifting of the distribution peaks towards each other. This feature of zeta potential distribution for a binary system suggests the absence of attraction forces between the two components, predicting at most a weak coagulation between bitumen droplets and clay particles to result in partial coating of montmorillonite or kaolinite clay particles on the surface of bitumen droplets.

- Figures 5-9c shows that in the presence of calcium ions, only one peak located at the position corresponding to the clay suspension, suggesting that clay completely coated the bitumen. This is an indication of a strong attraction for bitumen droplets that are covered with montmorillonite clay particles in the mixture.This study suggests that the coating of bitumen surfaces by hydrophilic montmorillonite clays results from the binding effect provided by calcium as bridge. This coating decreases the hydrophobicity of bitumen, resulting in the depression of bitumen recovery.

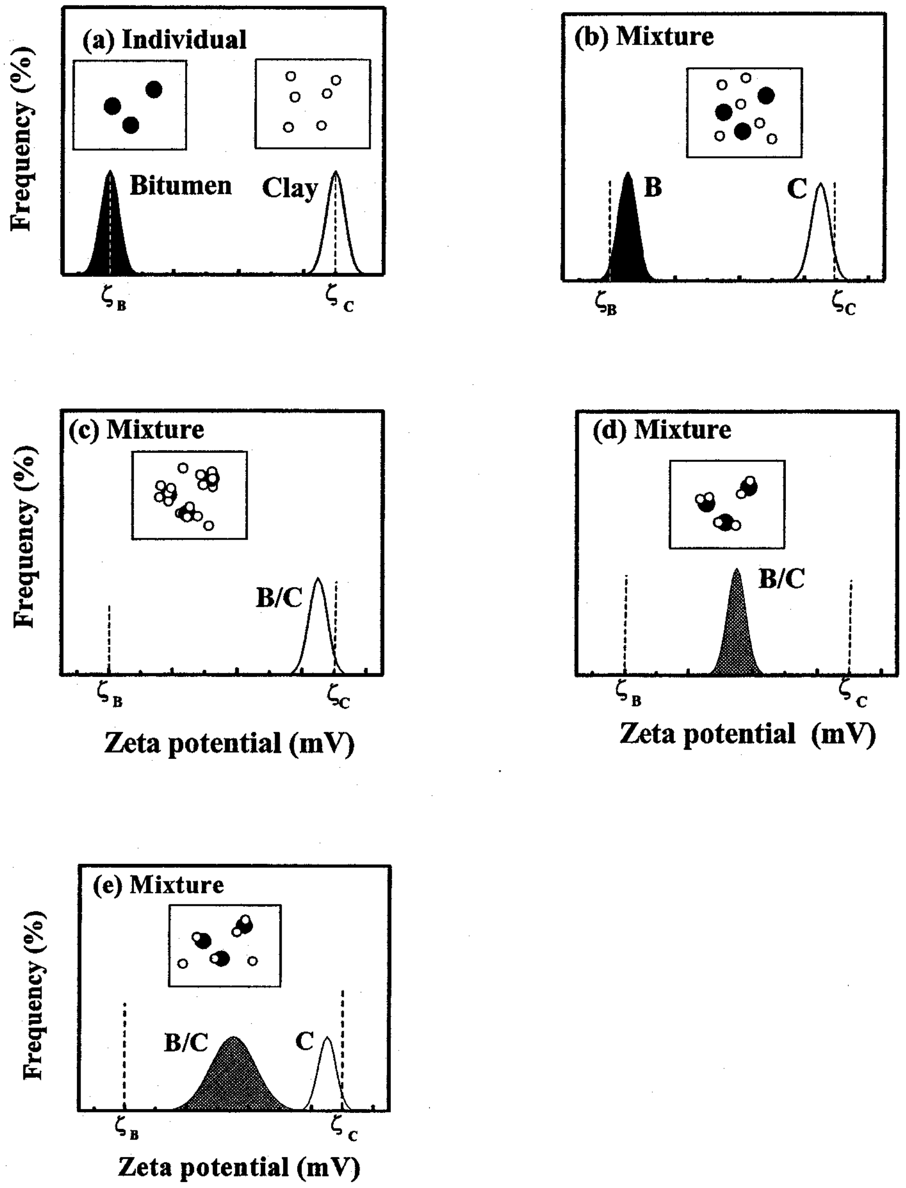

Figure 5-9: Schematic zeta potential distributions for a binary particulate component system, after Liu (2002)

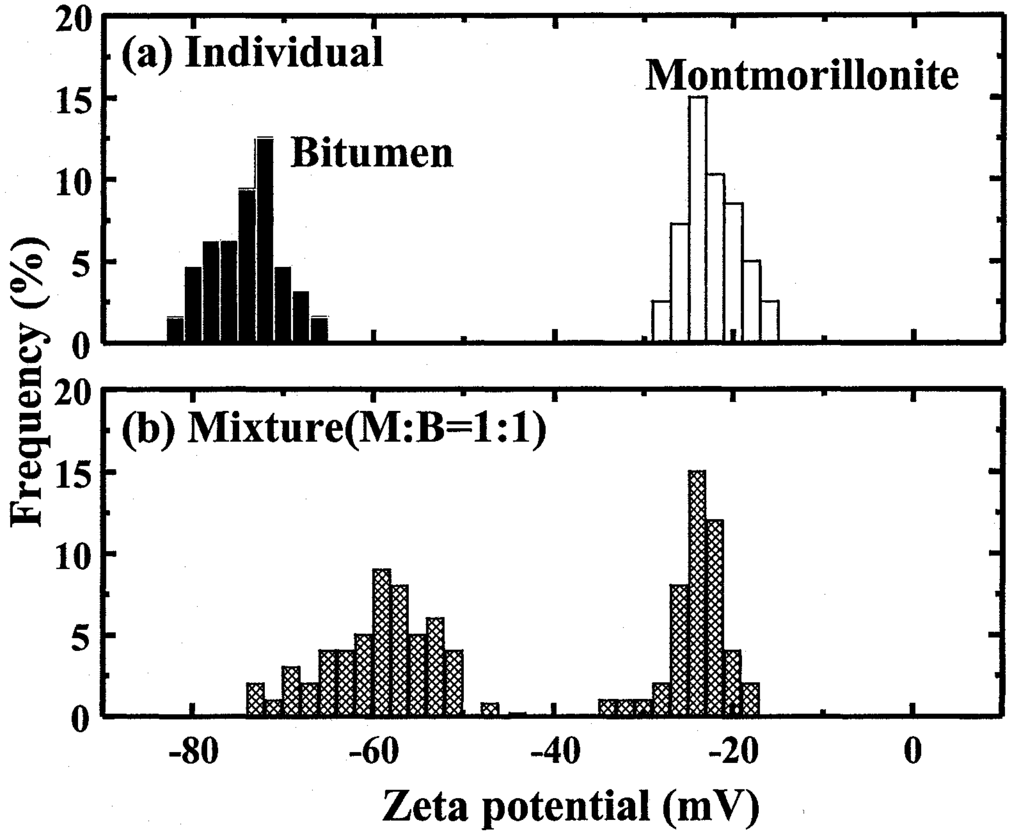

Figure 5-10: Zeta potential distributions for (a) individual bitumen drops and montmorillonite clay suspension and (b) their mixture at a pH of 8 in 1 mM KCl after Liu (2002)

- Figures 5-9(e) shows possible locations of peaks indicating weak attraction between bitumen droplets and clay particles that partially cover bitumen surface where a substantial amount of individual clay particles remain unattached to bitumen.

- Figure 5-13 (a to d) shows the increase of slime coating for kaolinite by increasing the kaolinite clay to bitumen mass ratios from 1:1 to 20:1 in the presence of calcium ions is shown in The results still show 2 peaks, suggesting that bitumen droplets are partially covered with clay particles, indicating a weak attraction in the mixture.

- Figure 5-14 shows results for bitumen froth and fines extracted from tailings slurries produced from a good processing ore sample.Zeta potential distributions have been used to study the effects of fine solids from ores that contain unknown amounts of clays on pure bitumen. The fine solids and bitumen were obtained by performing flotation tests and cleaning the froth with solvent.

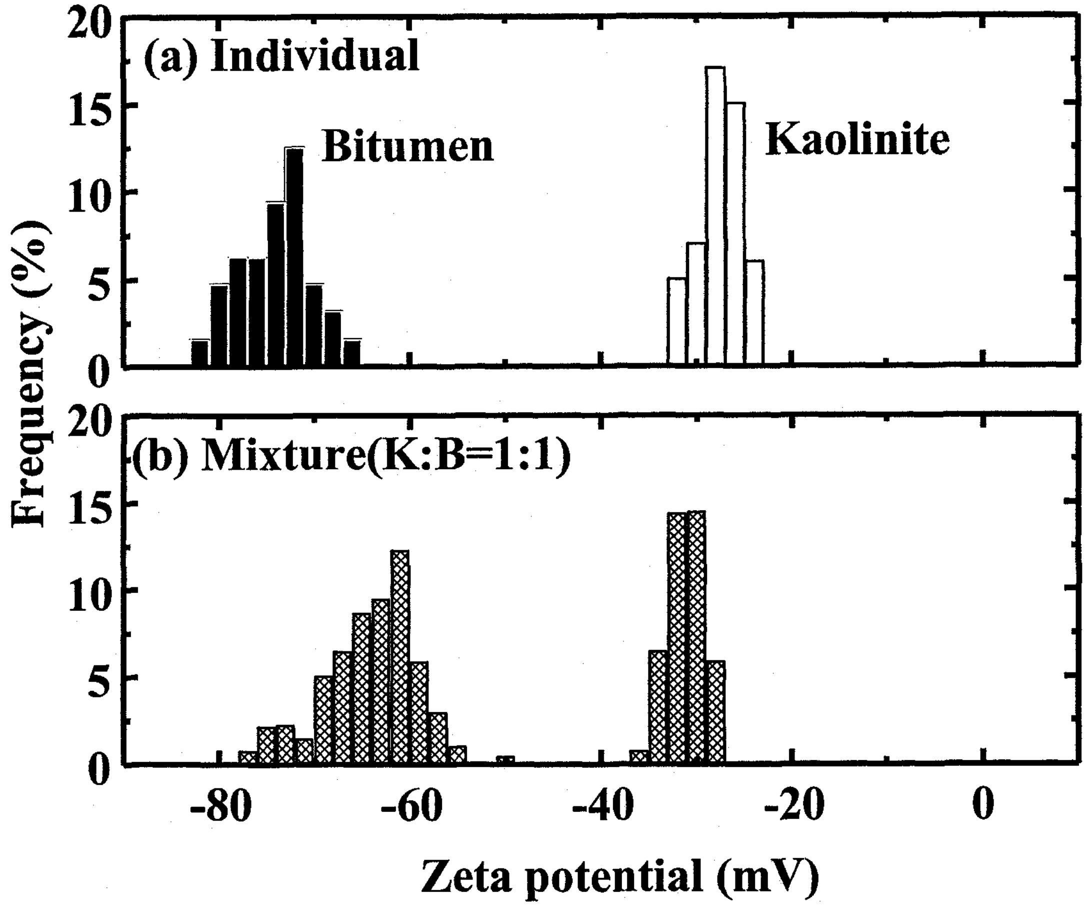

Figure 5-11: Zeta potential distributions for (a) individual bitumen drops and kaolinite clay suspension and (b) their mixture at a pH of 8 in 1 mM KCl after Liu (2002)

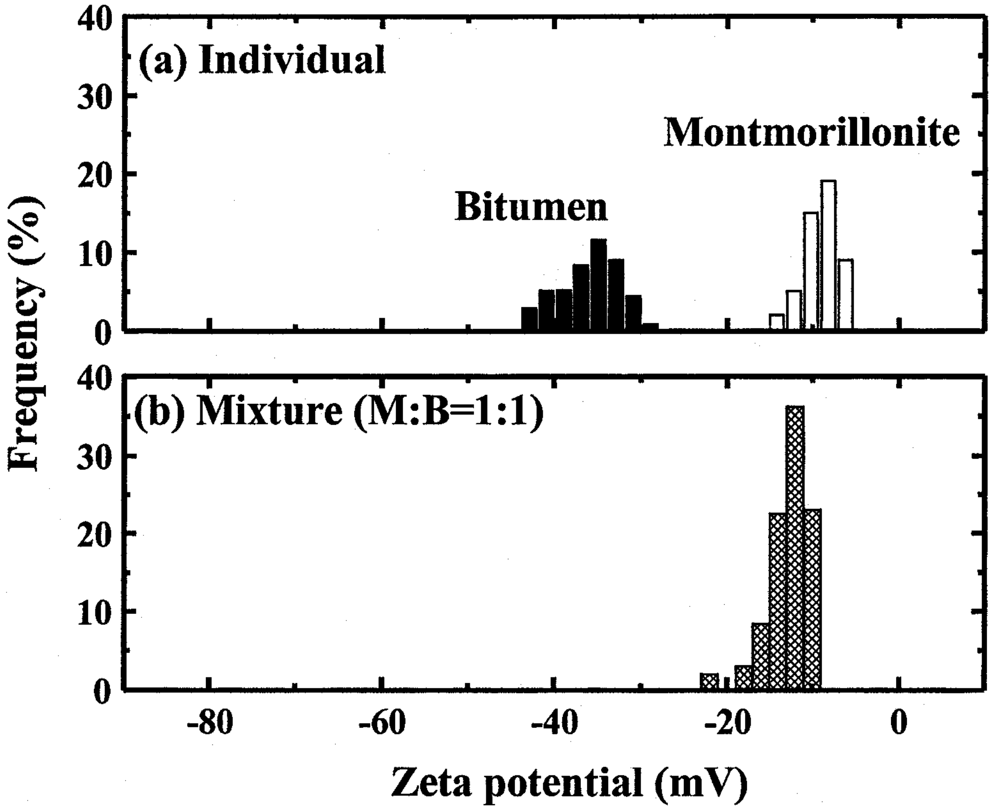

Figure 5-12: Effect of calcium addition on zeta potential distributions for (a) individual bitumen drops and montmorillonite clay suspension and (b) their mixture at a pH of 8 in 1 mM KCl with I mM calcium after Liu (2002)

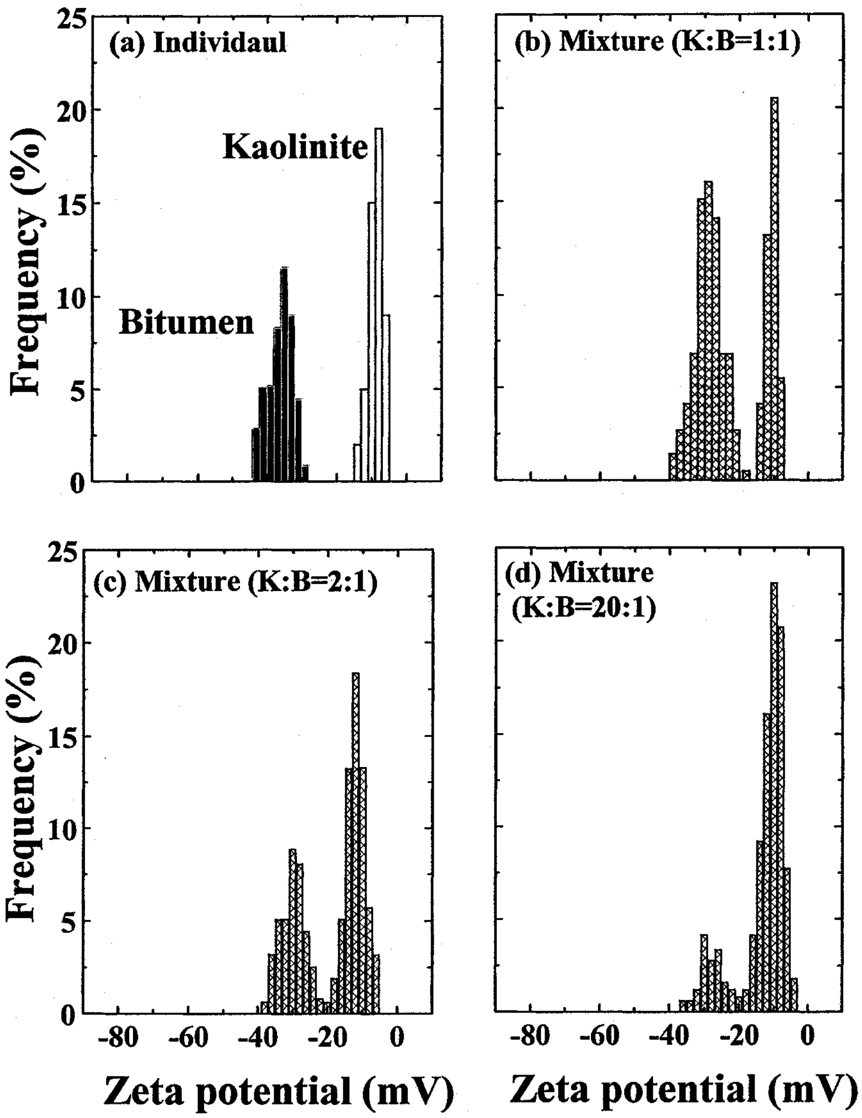

Figure 5-13: Effect of calcium and increasing kaolinite clays addition on zeta potential distributions for (a) individual bitumen drops and kaolinite clay suspension and (b,c,d) their mixture at a pH of 8 in 1 mM KCl with I mM calcium after Liu (2002)

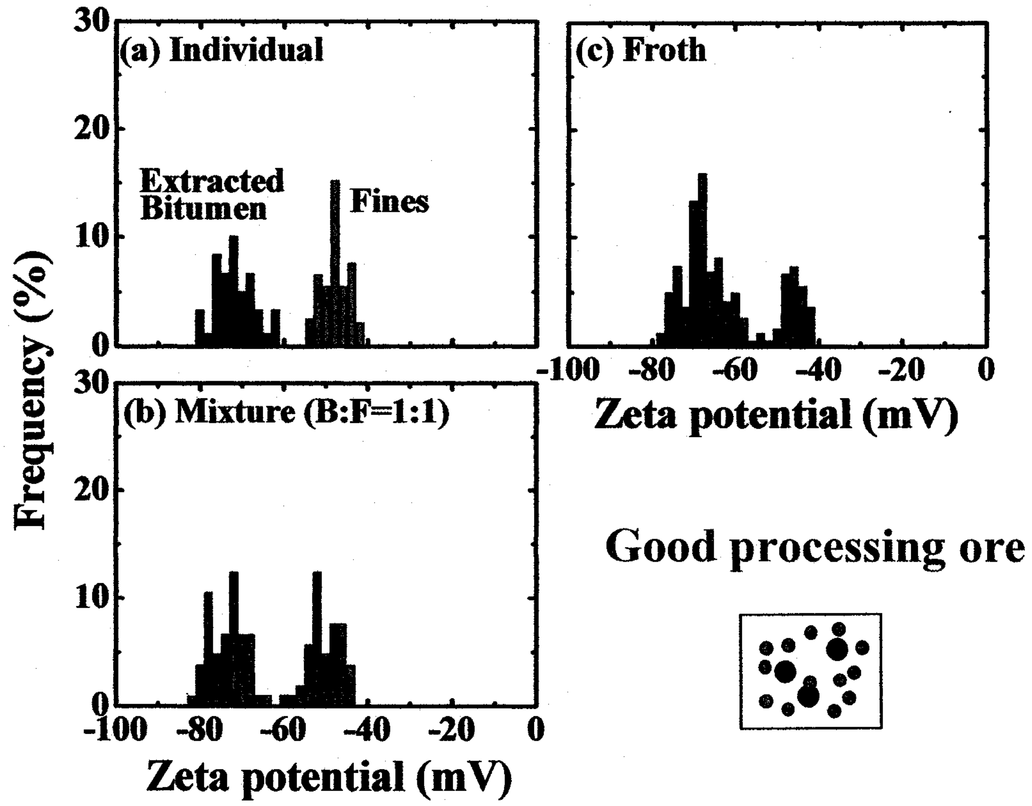

Figure 5-14: Good processing ore: zeta potential distributions for solvent extracted bitumen and fines: (a) individually, (b) mixture, (c) emulsified froth after Liu (2002)

- Figure 5-15 shows results for poor processing ore. For both cases, Figures 5-14(a) and 5-15(a) show zeta potential distributions for solvent extracted bitumen and fines extracted from their tailings slurries, measured separately.

- Figures 5-14(b) and 5-15(b) show the distributions of zeta potentials for the mixture of the solvent extracted bitumen and extracted fines. Figure 5-14(b) shows two separate peaks for good processing ores, but Figure 5-15(b) shows only one peak at the location of the distribution for fines produced from poor processing ore.

- These findings suggest the presence of coagulation and slime coating on bitumen of fines from poor processing ores but not from good processing ore. We observe the same effect in Figures 5-14(c) and 5-15(c) that show zeta potential distributions for emulsified froth from good and poor processing ores. The results of the emulsions confirm the results obtained in Figures 5-14(b) and 5-15(b) on slurries obtained by mixing pure bitumen with fines.

- The results confirm a weak interaction and absence of slime coating of fines on bitumen when both are produced from good processing ore, preserving the hydrophobicity of bitumen. Fines coagulate with the surface of bitumen when both are produced from poor processing ore, forming a slime coating that changes the bitumen surface to become less hydrophobic, resulting in weaker air bubble-bitumen attachment and poor bitumen recovery.

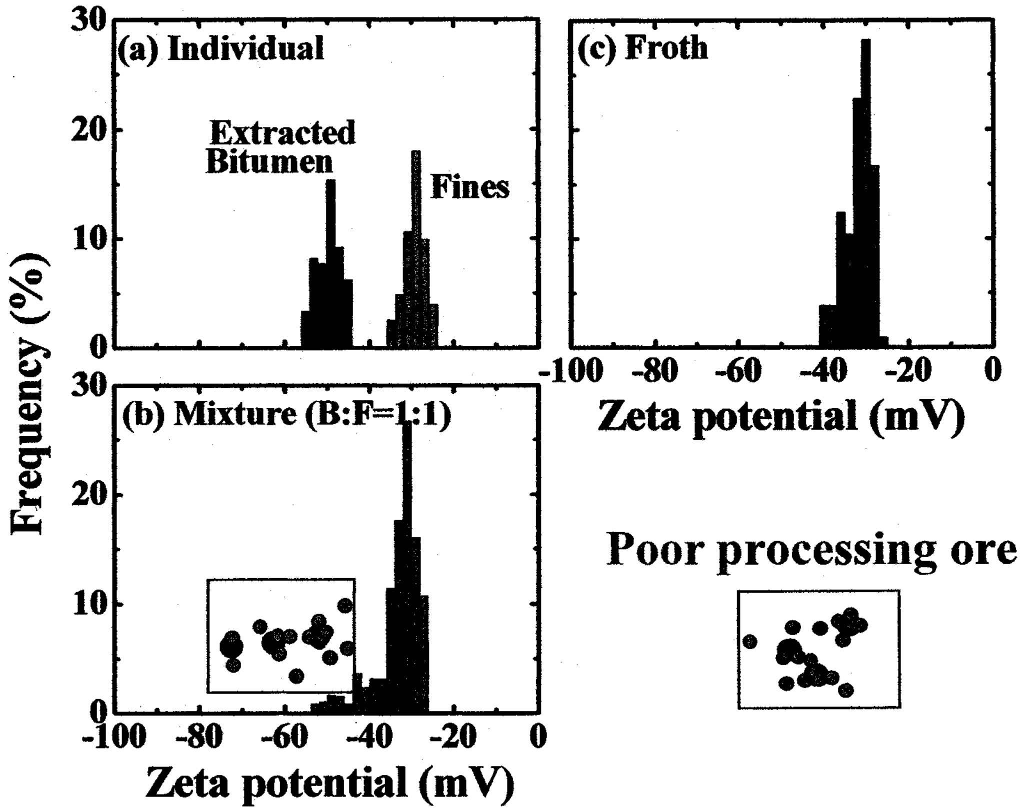

Figure 5-15: Poor processing ore: zeta potential distributions for solvent extracted bitumen and fines: (a) individually, (b) mixture, (c) emulsified froth after Liu (2002)

5.2 Atomic Force Microscopy Measurements (Lui et al., 2002

- Figure 5-16 shows the effects of slime coating. The slime coating effect was also studied by measuring the distribution of the adhesion force between montmorillonite clay andbitumen with and without calcium ions.

- Figure 5-16 shows that without calcium ions at pH 8.2, the adhesion force was centered at 4 mN/m. But with 1 mM calcium, it is stronger and centered at 9 mN/m due to the bridging effect of calcium ions between bitumen and clay particles. This produces a bitumen surface that is coated with fines, decreasing its hydrophobicity and attachment to air bubbles and hence leading to a decrease in bitumen recovery.

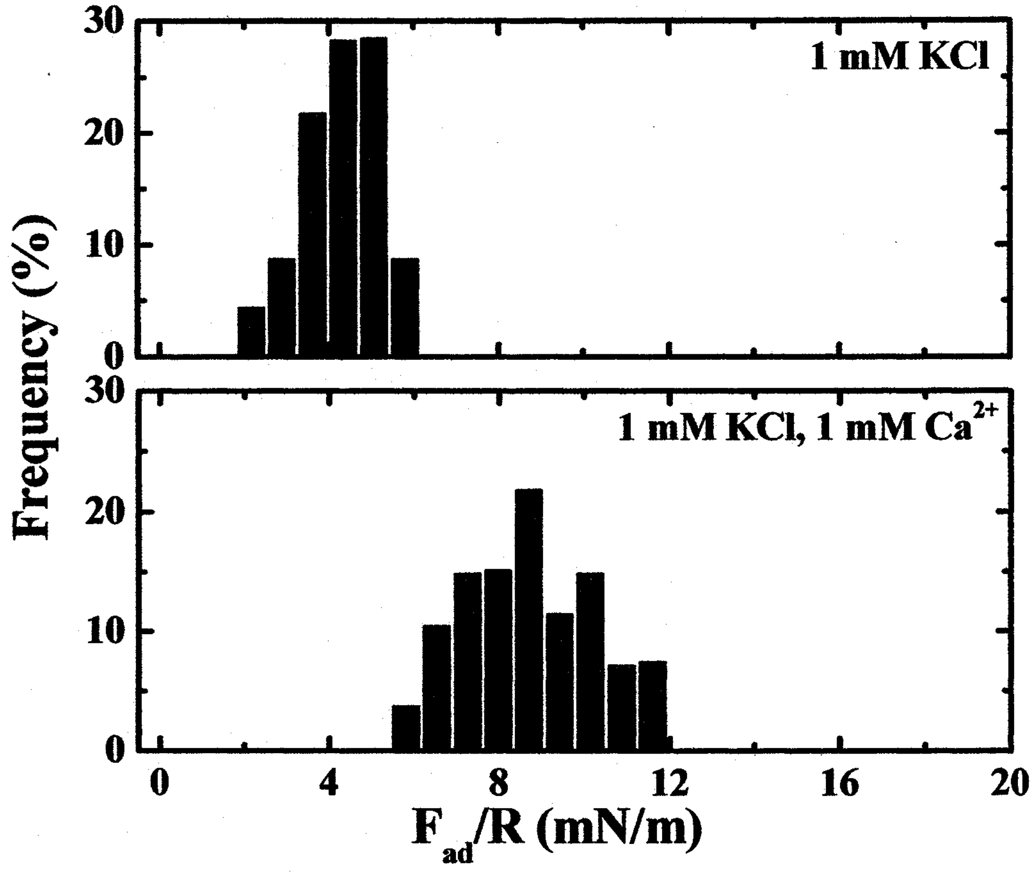

Figure 5-16: Effect of calcium addition on normalized adhesive forces between bitumen and montmorillonite clay in 1 mM KCl solution: (a) without calcium; (b) with 1 mM calcium after Liu (2003)

APPENDEX A6

Published papers:

Zhou, Z., T. Kasongo, Z. Xu and J. Masliyah: " Assessment of Bitumen Recovery from the Athabasca Oil Sands Using a Laboratory Denver Flotation Cell", The Can. J. Chem. Eng.,Vol. 82, 696-704, August 2004

Assessment of Bitumen Recovery from the Athabasca Oil Sands Using a Laboratory Denver Flotation Cell

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A methodology was developed in this study to evaluate the effect of operating parameters on the processability of oil sands using small-scale laboratory experimental devices. By subtracting bitumen recovered to the froth by entrainment with water, the concept of "true flotation recovery" is proposed to describe bitumen recovery resulting from bitumen-bubble attachment. The experimental results indicated that "true flotation recovery" is a more sensitive and meaningful marker than overall bitumen recovery to evaluate the processability of oil sands using small-scale laboratory test units.

Dans cette étude, on a mis au point une méthodologie pour évaluer l'effet des paramètres opératoires sur la capacité de traitement des sables bitumineux à l'aide de dispositifs expérimentaux de laboratoire de petite échelle. En retirant le bitume récupéré de la mousse par entraînement avec de l'eau, on propose le concept de « véritable récupération de flottation » afin de décrire la récupération de bitume résultant de la liaison bitume-bulles. Les résultats expérimentaux indiquent que la « véritable récupération de flottation » est un marqueur plus sensible et plus significatif que la récupération globale de bitume pour évaluer la capacité de traitement des sables bitumineux à l'aide d'unités d'essais de laboratoire de petite échelle.

Keywords: flotation recovery, bitumen flotation, Athabasca oil sands, water entrainment, poor processing ores.

Flotation is a surface wettability-based separation technology. It has been widely used for minerals and coal recovery, de-inking of recycled paper pulps, de-oiling, fine solids and ionic species removal from the industrial effluents (Gu and Chiang, 1999; Xu et al., 2001). For example, flotation has been used to recover heavy petroleum known as bitumen from Canadian Athabasca oil sands (Helper and Hsi, 1989; Hepler and Smith, 1994; Masliyah, 1994; Zhou et al., 2000). In processing Athabasca oil sand ores, the open-pit mined oil sands are conditioned in a tumbler or slurry pipelines with hot (80°C) or warm (50°C) water to liberate the bitumen from the sand grains. By attaching to or engulfing air bubbles, the liberated bitumen droplets are then floated to the top of the slurry in a primary separation vessel (PSV) to form a bitumen-rich froth. The bitumen remaining in the middlings is recovered using conventional mechanical flotation cells. The bitumen froth obtained as such normally contains 60% bitumen, 10% solids and 30% water, which is further processed with the addition of diluents to remove the entrained water and solids by centrifuges, cyclones and/or gravity settlers. The tailings are discharged from the bottom of the PSV and mechanical flotation cells to the tailings pond. The typical overall bitumen recovery in commercial operations is in the range of 85-94%.

To improve oil sands processability, reduce operating costs and minimize greenhouse gas emission, efforts have been devoted to developing process alternatives and considerable progress has been made as demonstrated by developing such processes as OSLO cold water extraction process (Sury, 1990, 1992; Hepler and Smith, 1994; FTFC, 1995) and Syncrude low energy extraction (LEE) process. Laboratory-scale techniques for investigating oil sand processability at lower extraction temperatures, however, have not kept in pace with commercial process development. The principal techniques for laboratory testing of oil sands processability over the years have been the beaker or jar tests (Bichard, 1987) and by the Batch Extraction Unit (BEU) developed at the Syncrude Canada Ltd (Sanford and Seyer, 1979). The BEU tests were used to simulate the Clark Hot Water Extraction (CHWE) process commercially operating at Syncrude Canada Ltd., Suncor Energy Inc. and Albian Sands Energy Inc. A great deal of the knowledge on oil sands processability has been derived from the thousands of experiments conducted with this unit. However, when the extraction temperature drops below 50°C, BEU tests become less sensitive and not as effective to detect the effect of operating parameters on bitumen recovery. In addition, with the recent development of slurry hydrotransport and continuous slurry aeration in the pipelines, novel laboratory experimental methodologies have to be developed to better understand fundamentals and extraction mechanisms involved in new extraction processes of industrial operations. The effort in this line of thinking led to the use of laboratory Denver flotation cells (Sury, 1990, 1992; Kasongo et al., 2000) and the development of a laboratory hydrotransport slurry pipeline (Wallwork, 2003; Wallwork, et al., 2003), among other techniques.

With the adoption of these new laboratory testing tools, correct interpretation of experimental data becomes increasingly critical, especially for testing poor processing ores containing less than 8% bitumen and a relatively high level of solid fines (say, > 20 wt%

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of solids in −44 µm size fractions). In this case a substantial amount of processing water along with entrained fines and bitumen are recovered to the froth. Since bitumen has a similar density to water, it has to be questioned whether the recovered bitumen is due to its attachment to air bubbles or entrainment in the water reporting to the froth. In the worst case, it may even provide misleading information if the data are not analyzed properly. It has been found that among other factors, bitumen recovery from oil sands also depends on the size and configuration of the extraction units used with different operators in different laboratories (Majid et al., 1982). Reconciliation of the difference in the experimental findings from processing the same type of oil sand ores remains a challenge. In this communication, a methodology was developed to evaluate the factors affecting bitumen flotation recovery. A concept of true flotation recovery was introduced to account for the bitumen recovery resulting from attachment to air bubbles. Experimental results in a laboratory Denver flotation cell indicated that true flotation recovery was a more sensitive marker to the changes in operating parameters or ore characteristics than the overall flotation recovery as conventionally used.

True Flotation Recovery

In recovering bitumen from Athabasca oil sands using water-based extraction processes, the following factors can contribute to the overall bitumen recovery to froth: a) bitumen recovered by attaching to air bubbles and then carried by the rising bubbles to the froth; and b) bitumen recovered by entrainment in the water reporting to the froth. Since bitumen has a similar density to the water in the temperature range commonly used in oil sands processing (Camp, 1976; Basu et al., 1996), recovery of bitumen by attaching to air bubbles should be a predominant mechanism for bitumen recovery. This portion of the recovered bitumen represents the true flotation recovery. Because of its similar density to water, bitumen can also be carried over to froth with the process water reporting to the froth. The recovery of slurry water to the froth is a known phenomenon in minerals flotation. This is mainly attributed to the rising bubbles carrying a water film with them and the entrained water in the bubble wake. The amount of water carried by the bubbles to the froth is a function of slurry physicochemical conditions with a stable froth retaining more water. Therefore, any particulates with minimal gravity or inertia effect present in the water film or the bubble wake could be carried over to the froth. Recovery of ultrafine hydrophilic particles with sizes less than 5 µm to the froth due to the water entrainment is a typical example in minerals flotation, unless a wash-water is added as practiced in column flotation to suppress the slurry water. The recovery of these hydrophilic particles is found to correlate well with water recovery. Since bitumen has similar density to water, its recovery to the froth by water entrainment could be significant. In bitumen extraction processes, the water reporting to the froth can be in different forms. At an operating temperature greater than 50°C, some water in the form of water-in-oil emulsion may also contribute to overall water recovery to the froth. For extraction tests at temperatures between 25 to 50°C, this portion of water reporting to the froth is marginal and could be ignored. As a result, all the slurry water reporting to the froth could be considered to carry entrained bitumen.

In laboratory studies, especially for poor processing ores, the amount of water reporting to the froth could be significant. It is therefore necessary to differentiate contributions of bitumen recovery by water entrainment. The process water reported to the froth carries not only unattached fine bitumen droplets, but also fine solids into the froth, thereby reducing bitumen froth quality. It is therefore desirable to minimize water recovery to the bitumen froth.

To differentiate the bitumen recovery by attachment to air bubbles from entrainment by recovered process water, the following true bitumen recovery concept is introduced. The assumption here is that the unaerated bitumen is uniformly distributed in the slurry and follows water due to their small sizes and near-equal density to water. The overall bitumen recovery at time t (R_o) is defined as the mass ratio of bitumen in the froth (W_{Ft}) to the bitumen in the feed (W_0), i.e.,

$$R_o - \frac{W_{Ft}}{W_o} \tag{1}$$

This definition of R_o is conventionally used to represent bitumen recovery for almost all the previously reported extraction tests. For practical purposes, this measure of bitumen recovery is satisfactory. To more accurately describe bitumen flotation phenomena or assess bitumen recovery mechanisms, this definition appears to be inadequate for understanding extraction process. True flotation recovery (R_T) is defined as the mass ratio of bitumen in the froth resulting from bitumen attachment to air bubbles (W_b) to the bitumen in the feed, i.e.,

$$R_T = \frac{W_b}{W_0} \tag{2}$$

True flotation recovery R_T would be therefore more meaningful than R_o to describe the effect of operating parameters on bitumen recovery by bubble attachment mechanism. Since W_b in Equation (2) cannot be determined experimentally, the following indirect approach is used to obtain R_T, under different conditions.

Since the extraction process does not involve chemical reactions, the bitumen disappearing from the slurry in a flotation cell is expected to accumulate on the surface of bubbles, and carried away from the slurry to the bitumen froth. It is also assumed that the bitumen is uniformly dispersed in the slurry by mechanical conditioning. Therefore, the bitumen accumulation rate on the bubble surfaces, dC_b/dt, should be equal to the disappearance rate of the unattached (air-free) bitumen in the slurry, $-dC_{st}/dt$, i.e.,

$$\frac{dC_b}{dt} = -\frac{dC_{st}}{dt} \tag{3}$$

where C_b is the air-attached bitumen concentration and C_{st} is the air-free bitumen concentration in the slurry at time t. Both C_b and C_{st} are based on the water volume in the slurry.

The recovery of bitumen resulting from its attachment to air bubbles can then be written as

$$R_T = 1 - \frac{C_{st}}{C_0} = \frac{C_0 - C_{st}}{C_0} \tag{4}$$

If we know the bitumen concentration C_{st} in the slurry at time t, the recovery R_T can then be obtained. The bitumen concentration in slurry C_{st} is defined as:

$$C_{st} = \frac{W_{st}}{V_{st}} \tag{5a}$$

In the ideal case of no bitumen recovered by water entrainment or at zero water recovery, the change of water volume in the slurry phase can be considered negligible, i.e., $V_{st} = V_0$, where V_0 and V_{st} are the volume of the water phase in the cell at the beginning and time *t*, respectively. The bitumen concentration in the slurry at time *t*, C_{st}, can then be written as:

$$C_{st} = \frac{W_{st}}{V_{st}} = \frac{W_0 - W_{Ft}}{V_{st}} \tag{5b}$$

where W_{st}, W_0 and W_{Ft} are the mass of bitumen remaining in the slurry, in the feed and in the froth at time t, respectively. In the case of no bitumen entrainment with water reporting to the froth, $W_{Ft} = W_b$, which results in Equation (2).

However, in conventional flotation tests, a certain amount of water is always carried over to the froth by entrainment. In this case,

$$V_{st} = V_0 - V_{Ft} \tag{6}$$

and

$$W_{Ft} = W_b - W_{bwt} \tag{7}$$

where V_{Ft} and W_{bw} are the volume of water reporting to the froth and the mass of bitumen entrained in the water carried over to the froth at time *t*, respectively.

By inserting Equations (5b) and (6) into Equation (4), and rearranging, one obtains

$$R_T = 1 - \frac{C_{st}}{C_0} = 1 - \frac{W_{st}}{C_0 V_{st}} = 1 - \frac{W_0 - W_{Ft}}{\frac{W_0}{V_0}\left(V_0 - V_{Ft}\right)} = 1 - \frac{1 - R_o}{1 - R_w}$$

i.e., (8)

$$R_T = \frac{R_0 - R_w}{1 - R_w}$$

where R_w (= V_{Ft}/V_0) is the portion of slurry water that is recovered to the froth, known as water recovery.

Equation (8) indicates that the true bitumen flotation recovery due to its attachment to air bubbles is related to the overall bitumen recovery and water recovery. Since R_o and R_w are available using standard analytical procedures (Bulmer and Starr, 1979), R_T can therefore be determined readily. The relationship between true bitumen flotation recovery and water recovery, i.e., Equation (8), is plotted in Figure 1. For a given water recovery, the true bitumen flotation recovery becomes severely reduced for the case of a lower overall bitumen recovery. For an overall bitumen recovery of over 90%, the true bitumen flotation recovery is insensitive to a water recovery of up to 40%. In conventional oil sands extraction practice, bitumen recovery of over 90% can be obtained for a good processing ore containing a high bitumen content, but bitumen recovery of less than 70% is normally reported for a poor processing ore containing less than 8% bitumen and a relatively high fines content. The prediction from Equation (8) or Figure 1 would suggest a potential problem of interpreting flotation recovery for a poor processing ore at a relatively high water recovery. In this case, using true bitumen flotation recovery to assess ore processability is desired.

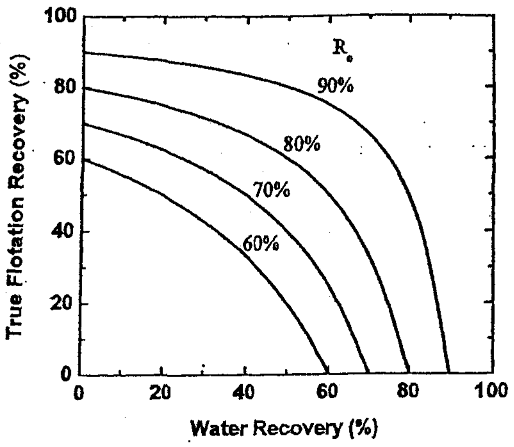

Figure 1. Prediction of water recovery effect on true flotation recovery by Equation (8).

Experimental

Two types of oil sand ores from Syncrude Canada, Ltd. were tested: a good processing oil sands ore containing 14.5% bitumen and a poor processing oil sands ore containing 7.5% bitumen. The compositions of these samples are given in Table 1. A distinct difference between the good and poor processing ores is a relatively high fine solids (–44 µm) content of more than 30% in poor processing ores. A laboratory 1-L Denver flotation cell was used to conduct the flotation tests. A water jacket connected to a temperature-control thermal bath was attached to the Denver cell to adjust the slurry temperature during flotation. Two different aeration procedures were compared. The first was staged-aeration similar to that used in BEU tests (Sanford and Seyer, 1979; Kasongo et al., 2000) to evaluate the processability of these two samples. In this case, 450 g of oil sands were conditioned with 300 mL of de-ionized water in the cell at 80°C for 5 min under a specified aeration rate of 150 mL/min. After the first 5-minute of agitation and aeration, 600 mL water (80°C) was added into the cell while it was under continuous agitation without aeration. Bitumen froth was then collected into different flotation time intervals for 10 min. For the convenience of discussion, this procedure is referred to as BEU test procedure.

In the second procedure, a continuous aeration scheme was used. In this case, 450 g of oil sands was mixed with 900 mL of water in the 1-L Denver cell, and conditioned at a given agitation speed for 5 min without air addition. Bitumen froth was then collected under continuous aeration at 150 mL/min, into different time intervals for 10 min. The bitumen, solids and water content in the froth products and the feed were analyzed using the standard Dean Stark method developed at the Syncrude (Bulmer and Starr, 1979). From the assay results, the bitumen and water recovery over a given flotation period

Table 1. Composition of testing samples (wt%)

	Bitumen	Water	Solids	Fines (%) (-44 μm)
Good ore	14.3–14.5	0.5–0.8	85.3–85.5	4
Poor ore	7.3–7.5	7.3–7.8	85.3–86.0	40

was calculated. We will refer to R_o as the overall flotation recovery and R_T as the true flotation recovery. Here the bitumen recovery presented by R_o includes both bitumen attached to air bubbles and that entrained by the water, whereas R_T represents bitumen recovery due to attachment to air bubbles only.

Results and Discussion

Effect of Aeration Procedures

To examine the processability of the oil sands in a conventional way, the BEU test procedure was first used. A first order disappearance kinetic model as shown below was used to evaluate overall bitumen recovery kinetics:

$$R_o = R_\infty(1 - e^{-kt}) \tag{9}$$

where R_o and R_∞ are the bitumen recovery at time t and ultimate bitumen recovery, respectively, and k is the bitumen flotation rate constant (min^{-1}). Equation (9) was found to fit the overall bitumen recovery data quite well as shown in Figure 2. Here both values of k and R_∞ were obtained simultaneously by the nonlinear least square method using the solver in Excel. The results in Figure 2 show that for the good processing ore, a fast bitumen recovery was observed. More than 90% bitumen was floated within 5 min with a flotation rate constant of 0.57 min^{-1}. While for the poor processing ore under the same flotation condition, the primary recovery over a 10 min period was only about 20%, with a flotation rate constant of 0.02 min^{-1}. The flotation rate constant in this case is more than 25 times less than that for the good processing ore. The observed difference of good and poor processing ores in responding to bitumen flotation has been well established by previous researchers using BEU testing procedures (Sanford, 1983; Schramm et al., 1984). The results showed that bitumen can be recovered readily from good processing ores. However, for poor processing ores, it is difficult to recover bitumen in the conventional BEU tests or in industrial Clark Hot Water Extraction (CHWE) process without adding any process aids.

Considering that the bitumen was collected after stopping agitation and aeration, this mode of froth collection is anticipated to minimize the recovery of process water. As a result, the bitumen recovery resulting from water entrainment can be considered to be minimal using the BEU procedure, although attention was not paid previously to the issues of bitumen recovery by water entrainment. The similar values of true flotation recovery to overall recovery suggest that bitumen recovery from oil sands slurry using BEU tests at 80°C was predominantly by collecting bitumen droplets attached to air bubbles. The low bitumen recovery from poor processing ores is therefore indeed due to poor bitumen-bubble attachment. The suitability of using the overall bitumen recovery from BEU tests to interpret bitumen-bubble attachment during extraction is therefore justified.

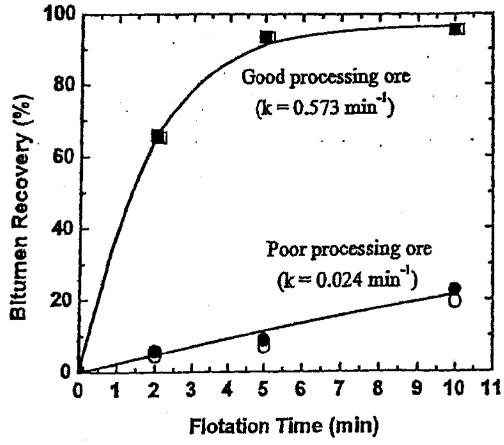

Figure 2. Comparison of good processing ore and poor processing ore flotation using BEU procedure in a Denver cell (1800 rpm; 80°C; Solid line: curve fitting from Equation 9)

Solid symbol: overall flotation recovery;
Open symbol: true flotation recovery.

To examine the processability and improve the bitumen-bubble attachment for the poor processing ore, the continuous aeration procedure was compared with staged aeration procedure in flotation tests using the same Denver cell. The results in Figure 3 show a much higher overall bitumen recovery (solid symbols) with continuous aeration than that with the staged-aeration procedures. For a 10 min flotation period, for example, continuous aeration resulted in a bitumen recovery of 75% in comparison to 22% with staged aeration. While it may be argued that at the same aeration rate, the actual amount of air input in the continuous aeration procedure was higher, the continuous aeration procedure over a five-minute period resulted in a much higher bitumen recovery of 61%, in comparison to 9% obtained by staged-aeration procedure over the same period during which the total volume of air introduced was the same for these two procedures. The results appear to suggest that the staged aeration procedure was not as effective for bitumen-air attachment as the continuous-aeration for recovering bitumen from the poor processing ore. A distinct difference between the two procedures is a significant increase in process water recovery to the froth by continuous aeration. Therefore, the increased overall bitumen recovery by continuous-aeration procedure could be partially accounted for by bitumen entrainment in the increased process water recovered to the froth. Nevertheless, after correction for water recovery, true bitumen recovery by attachment to air bubbles (open symbols) using the continuous aeration procedure was still more than double of that obtained with the staged aeration. This finding suggests that continuous aeration is indeed more effective in enhancing bitumen-bubble attachment than staged aeration.

One possible reason for poor bitumen recovery by the staged-aeration procedure could be due to a much higher solids-to-water ratio used in the conditioning and aeration

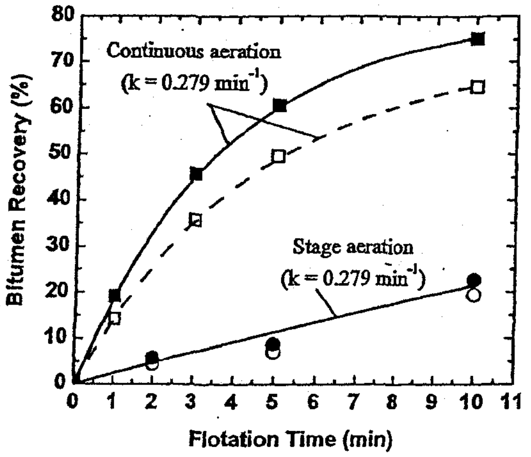

Figure 3. Effect of different aeration procedures on bitumen flotation using Denver cell (poor processing ore: 7.5% bitumen. $T = 80°C$; 150 mL/min air; 1800 rpm. Solid and dashed lines: curve fitting from Equation 9). Solid symbol: overall flotation recovery; open symbol: true flotation recovery.

stage. Although the same amount of air was introduced into the extraction system for both procedures, it is the efficiency of air dispersion, or the amount and size of bubbles generated in the system that determine the bitumen-bubble contact frequency. It is conceivable that the presence of a higher content of fines in the poor processing ores causes a more viscous slurry, thereby interfering with the air dispersion and bitumen-bubble attachment. More concentrated slurry also makes the slurry contain a higher concentration of natural water soluble surfactant released from ores. As a result, the bubbles are more quickly aged (loaded with surfactant) and become less effective for collecting bitumen droplets. For this reason, the continuous aeration procedure was used in all the tests described below, unless otherwise specified.

Effect of Operating Parameters

Temperature

Temperature has a significant impact on improving bitumen liberation from sand grains, accelerating bitumen attachment to air bubbles and hence enhancing bitumen flotation. Figure 4 shows the effect of temperature on bitumen recovery for the two types of oil sand ores. For the good processing ore (Figure 4a), a significant enhancement of bitumen flotation kinetics by increasing the processing temperature from 25 to 50°C was observed. The flotation rate constant increased from 0.15 min^{-1} at 25°C to 0.98 min^{-1} at 50°C. When the temperature was higher than 50°C, increasing the processing temperature showed virtually no further effect on bitumen recovery. A similar finding was reported by Bichard (1987) who noted that over a temperature range of 50 to 90°C, the temperature showed little effect on bitumen recovery. Recent work by Schramm et al. (2003) using BEU tests also demonstrated a similar trend in terms of temperature effect on bitumen recovery. Collectively, the results suggest that for the good processing ore, using warm water (50°C) is sufficient to reach a maximum bitumen recovery. This finding is in line with current directions of commercial operations in the oil sands industry. For this reason, further tests were conducted at a temperature of 50°C or less.

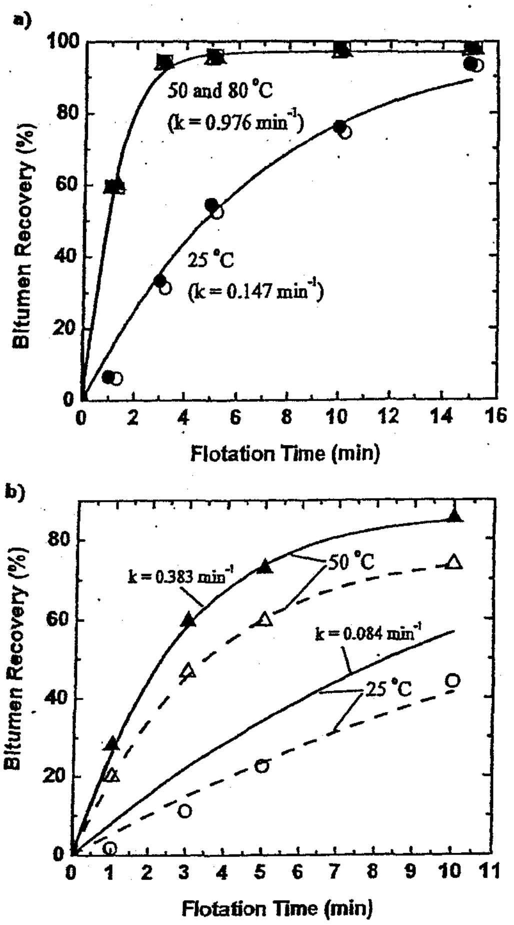

Figure 4. Effect of temperature on bitumen flotation using a Denver cell (150 mL/min air, 1800 rpm. Solid and dashed lines: curve fitting from Equation 9). a) Good processing ore and b) Poor processing ore.

Figure 4a also shows that for a given operating temperature, the difference between the overall (solid symbol) and true bitumen recovery (open symbol) is not significant, as justified by similar flotation recoveries obtained for a given temperature. This finding suggests that the predominant bitumen recovery mechanism for the good processing ore was by bitumen-air bubble attachment.

For the poor processing ore, however, different flotation behavior was observed. Figure 4b also shows an increase in the overall bitumen recovery with temperature from 25 to 50°C. However, the true flotation recovery was much lower than the overall recovery, especially at lower temperatures, suggesting that a significant amount of bitumen was recovered due to water entrainment. Over a 10 min flotation period at 25°C, for example, the overall recovery was ca. 58% in comparison to 44% of true flotation recovery. Compounded with a low bitumen recovery from poor processing ores is a higher water recovery when compared with good processing ores. As a result, using true bitumen flotation recovery to assess processability of poor processing ores and understanding bitumen recovery mechanism become increasingly important, as indicated by the theoretical considerations shown in Figure 1. Therefore, only the results of poor processing ores will be presented and discussed below.

Oil Sands to Water Ratio

To illustrate the shortcomings of using overall bitumen recovery as an indicator for oil sands processability, the effect of slurry density, i.e., oil sands ore to water mass ratio on bitumen extraction was investigated. Figure 5 shows little effect of changing oil sands ore to water mass ratio on the overall bitumen recovery obtained over a 10-min flotation time. However, an increasing trend in true bitumen flotation recovery with reducing oil sands ore to water mass ratio is evident. The results here suggest that suitable dilution of oil sands feed slurry could be a viable means to improve bitumen-air attachment efficiency. However, excessive dilution is not recommended as it limits the capacity of process equipment, or otherwise reduces the residence time that can offset any improvement in bitumen-air attachment. A similar observation was made in BEU tests by Takamura and Wallace (1988). As demonstrated earlier, using the overall bitumen recovery from BEU tests was suitable to interpret bitumen recovery by bubble attachment. Their finding is consistent with our approach of comparing true bitumen recovery.

Caustic Addition

It is clear that one of the key issues in improving processability of poor processing ores is to minimize the deposition of fine solids on bitumen (Liu et al., 2002, 2003). One practical approach is to increase repulsive energy barriers between fine solids and bitumen surface by caustic addition. To further illustrate the possible limitation of using overall bitumen recovery at a fixed flotation time for evaluating ore processability, the effect of caustic addition on bitumen recovery was examined. The results in Figure 6 show that the overall bitumen recovery remained similar at 10-min flotation time with caustic addition. Based on such results, one might conclude that caustic addition has little effect on bitumen recovery. This conclusion is contrary to practical experience of the improved processability by caustic addition in both industrial operations and laboratory scale BEU tests. Further analysis showed a significant increase by 10% in true bitumen flotation recovery with a 0.04 wt% (of oil sands) caustic addition. One role of adding caustic in the slurry is to disperse fine solids, thereby minimizing fine solids deposition on bitumen surface. In addition, dispersing fine solids makes the bubbles and the formed froth less rigid and stable, facilitating the drainage of entrained water by bubble coalescence. This is in line with the observed reduction of water recovery with caustic addition, resulting in a better froth quality.

It should be noted that a similar trend was observed from the tests with other poor processing ores containing high fines content (e.g., Syncrude Aurora transition ores). The analysis of true flotation recovery led to a general trend consistent with previously reported observations, illustrating the value of using true bitumen flotation recovery in evaluating processability of oil sands by a laboratory scale unit.

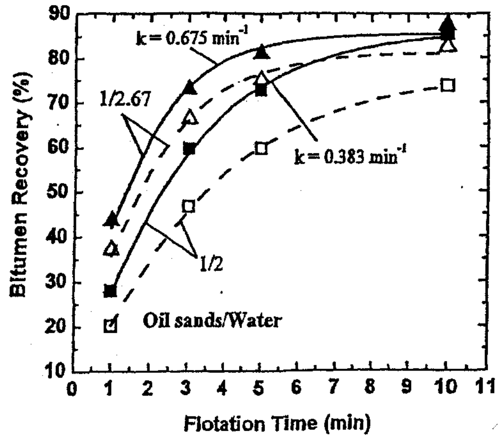

Figure 5. Effect of oil sands/water ratio on bitumen flotation from poor processing ores using a Denver cell ($T = 50$°C, 150 mL/min air, 1800 rpm. Solid and dashed lines: curve fitting from Equation 9). Solid symbol: overall flotation recovery; open symbol: true flotation recovery.

Practical Implications

Laboratory tests are the first step for developing a new or modifying any existing industrial process. They are often used to screen chemical additives or determine critical operating conditions, such as temperature, pH, and tolerance level of interfering species. Therefore, correctly interpreting laboratory flotation results could have a significant impact on decision-making at pilot and commercial scale operations. In bitumen recovery from oil sand ores, for example, bitumen attachment to air bubbles is critical for bitumen recovery. Any factors which hinder the bitumen-bubble attachment would depress bitumen recovery. The amount of process water recovered in the froth determines, to a certain degree, the froth quality.

The results presented in this work demonstrate the importance of using a true flotation recovery, as opposed to the use of conventional overall flotation recovery over a fixed flotation period as a marker in evaluating the effect of operating parameters or ore characteristics on the processability of oil sand ores. By applying this concept to bitumen extraction, it is confirmed that the dominant bitumen recovery mechanism in BEU tests is by bitumen-bubble attachment. For the good processing ore, bitumen recovery by water entrainment is negligible. However, for poor processing ores of low bitumen and high fines content, caution has to be taken when using the overall bitumen recovery as a marker with a small-scale laboratory test unit.

Although bitumen recovery using staged-aeration procedure as in BEU tests can be considered as true flotation, the extremely low bitumen-bubble attachment efficiency and low recovery would not reflect the flotation environment in mechanical flotation cells. Therefore, this method does not

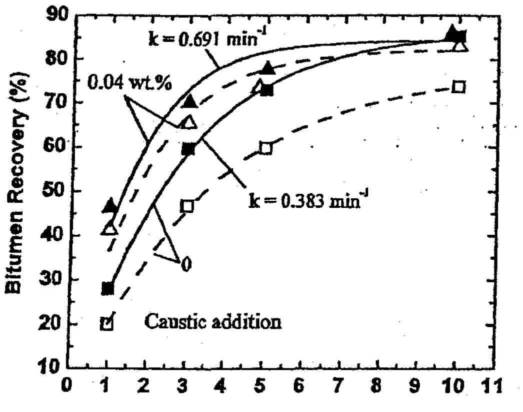

Figure 6. Effect of caustic addition on bitumen flotation from poor processing ores using a Denver cell ($T = 50$ °C, 150 mL/min air, 1800 rpm. Solid and dashed lines: curve fitting from Equation 9). Solid symbol: overall flotation recovery; open symbol: true flotation recovery.

appear to be suitable for assessing the effect of physical parameters on bitumen recovery and developing strategies for improving the processability of poor processing ores, especially with low temperature (< 50°C) processes. In this regard, continuous aeration as used in mineral flotation seems to provide a better bitumen-bubble attachment environment. Indeed, the commercial oil sands operations are now shifting to use continuous feed slurry aeration in hydrotransport pipelines.

Flotation is a rate process in a sense that the flotation recovery of targeted hydrophobic entities by bubbles is time-dependent. In general, the longer is the flotation time, the higher is the recovery, until reaching a maximum plateau. Therefore, comparing the flotation performance using a single recovery value over a given flotation period suffers a disadvantage that the rate component of the recovery process may be hidden. The results and interpretation in this case are very much dependent on the flotation time chosen. When the selected flotation time is too long that the flotation recovery reaches the maximum plateau, the recovery becomes independent of the processing conditions. This may explain why sometimes the previously designed experimental procedures, such as the Syncrude BEU test of 10-minute froth collection is not sensitive to detect the effect of chemical addition or other variables on oil sands processability. The results from our study (see Figures 4a, 5 and 6) also demonstrated that depending on the selection of flotation time, different conclusions could be drawn as to the effect of temperature, oil sands to water ratio and caustic addition on bitumen recovery. For example, if bitumen flotation time is limited to 5 minutes or shorter (Figures 4a, 5 and 6), a significant impact of increasing process temperature, reducing oil sands to water mass ratio or adding caustic on increasing bitumen recovery becomes evident. However, for a froth collection time longer than 10 min, no temperature (or oil sands to water ratio and caustic addition) effect could be observed on the overall bitumen recovery. The results suggest that using a single bitumen recovery value at a given flotation time, as practiced by almost all of the previous studies, may not be adequate to reflect bitumen recovery process. Considering flotation being a rate process, using flotation rate constant to assess ore processability would be more appropriate. As shown in Figure 4a, flotation rate constant increased significantly from 0.15 min^{-1} at 25°C to 0.98 min^{-1} at 50°C. Proper dilution of oil sands slurry (Figure 5) increased bitumen flotation rate constant from 0.38 min^{-1} at 1:2 oil sands/water ratio to 0.67 min^{-1} at 1:2.67 oil sands/water ratio. For caustic addition at 0.04wt% ores processed, a double in bitumen flotation rate constant was obtained as compared with the case without caustic addition. These general trends are in line with the trends derived by comparison of true bitumen recovery, but not overall bitumen recovery over a 10-minute froth collection. It is clear that true flotation recovery and/or flotation rate constant is a better indicator to assess ore processability or process performance using different laboratory test units and experimental procedures. While the true flotation recovery serves satisfactorily for the purpose of understanding how the operating parameters affect bitumen-bubble attachment, the value of flotation rate constant can be used to evaluate how effectively the different ores respond to the adopted extraction processes.

It should be mentioned that although the developed methodology in this work is focused on bitumen extraction from oil sands, it is also applicable to flotation recovery of fine particles and precipitates where the gravity or inertia effect may be minimal, and where water recovery is significant in a small scale laboratory unit, such as Hallimond tube or mechanical flotation cells.

Conclusions

1. A new concept of true flotation recovery is introduced to assess the effect of operating parameters on bitumen recovery by bitumen-bubble attachment.
2. Bitumen recovery using conventional staged-aeration procedure in a BEU was found to be predominantly by bitumen-air bubble attachment.
3. When processing a good processing oil sand ore, bitumen recovery was mainly due to bitumen-air bubble attachment. However, when processing a poor processing ore, both bitumen-air bubble attachment and bitumen entrainment in water contributed to overall bitumen recovery.
4. True flotation recovery is a more sensitive and meaningful marker than overall bitumen recovery to evaluate oil sands ore processability in terms of bitumen-bubble attachment mechanism, using a small-scale laboratory apparatus.
5. A better strategy to assess bitumen extraction performance or bitumen-bubble attachment efficiency in different laboratory units with different experimental procedures is to compare true flotation recovery and/or flotation rate constant.

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Nomenclature

C_0	initial concentration of bitumen in the slurry, (kg/m^3)
C_b	concentration of air-attached bitumen in the slurry, (kg/m^3)
C_{st}	non-air attached bitumen concentration in the slurry at time t, (kg/m^3)
k	rate constant for overall bitumen flotation rate constant, (min^{-1})
R_o	overall bitumen recovery at time t
R_T	true bitumen flotation recovery due to bitumen-bubble attachment
R_w	water recovery in the froth
R_∞	bitumen recovery at time infinity
V_0	initial volume of water added in the slurry, (m^3)
V_{Ft}	volume of water reporting to the froth, (m^3)
V_{st}	volume of water in the slurry at time t, (m^3)
W_0	weight of bitumen in the feed, (kg)
W_b	weight of bitumen in the froth resulting from bitumen attachment to air bubbles, (kg)
W_{bw}	weight of bitumen entrained in water carried over to the froth at time t, (kg)
W_{Ft}	weight of bitumen in the froth at time t, (kg)
W_{st}	weight of bitumen remaining in the slurry at time t, (kg)

References

Basu, S., K. Nandakumar and J. Masliyah, "A Study on Oil Displacement on Model Surfaces", J. Colloid Interface Science, 182, 82–84 (1996).

Bichard, J.A., "Oil Sands Composition and Behavior Research", The research papers of John A. Bichard 1957-1965, AOSTRA technical publication series 4, Alberta Oil Sands Technology and Research Authority, Edmonton, AB (1987).

Bulmer, J.T. and J. Starr, "Syncrude Analytical Methods for Oil Sand and Bitumen Processing" AOSTRA technical publication series #1, Alberta Oil Sands Technology and Research Authority, Edmonton, AB (1979).

Camp, F.W., "The Tar Sands of Alberta, Canada", 3rd ed., Cameron Engineers, Inc., Denver, CO, (1976).

FTFC (Fine Tailings Fundamentals Consortium), "Advances in Oil Sands Tailings Research", AOSTRA, Edmonton, AB (1995).

Gu, X. and S. H. Chiang, "A Novel Flotation Column for Oily Water Cleanup", Sepa. Puri. Tech., 16, 193–203 (1999).

Hepler, L.G. and C. Hsi, "AOSTRA Technical Handbook on Oil Sands, Bitumen and Heavy Oils", AOSTRA technical publication series #6, Alberta Oil Sands Technology and Research Authority, Edmonton, AB (1989).

Hepler, L.G. and R.G. Smith, "The Alberta Oil Sands: Industrial Procedures for Extraction and Some Recent Fundamental Research", AOSTRA technical publication series #14, Alberta Oil Sands Technology and Research Authority, Edmonton. AB (1994).

Kasongo, T., Z. A. Zhou, Z. Xu and J. H. Masliyah, "Effect of Calcium Ions and Fine Clays on Bitumen Extraction from Athabasca Oil Sands Using Flotation", Can. J. Chem. Eng. 78, 674–681 (2000).

Liu, J., Z. Xu and J. Masliyah, " Studies on Bitumen-Silica Interaction in Aqueous Solutions by Atomic Force Microscopy", Langmuir 19, 3911–3920 (2003).

Liu, J., Z. Zhou, Z. Xu and J. Masliyah, "Bitumen-Clay Interactions in Aqueous Media Studied by Zeta Potential Distribution Measurement". (J. Colloid and Interface Science) 252, 409–418 (2002).

Majid, A., A.F. Sirianni and J.A. Ripmeester, "Comparative Study of Three Laboratory Methods for the Extraction of Bitumen from Oil Sands", Fue 61, 477–479 (1982).

Masliyah, J.H., "Electrokinetic Transport Phenomena", AOSTRA Technical Publication Series #12, Edmonton, AB (1994).

Sanford, E.C. and F.A. Seyer, "Processibility of Athabasca Tar Sand Using a Batch Extraction Unit: The Role of NaOH", CIM Bull. 72, 164–169 (1979).

Sanford, E.C., "Processibility of Athabasca Oil Sand: Interrelationship between Oil Sand Fine Solids, Process Aids, Mechanical Energy and Oil Sand Age After Mining", Can. J. Chem. Eng. 61, 554–567 (1983).

Schramm, L.L., R.G. Smith and J.A. Stove, "The Influence of Natural Surfactants Concentration on the Hot Water Process for Recovering Bitumen from the Athabasca Oil Sands", AOSTRA J., 1, 5–13 (1984).

Schramm, L.L., E.N. Stasiuk, H. Yarranton, B.B. Maini and B. Shelefantook, "Temperature Effects from the Conditioning and Flotation of Bitumen from Oil Sands in Terms of Oil Recovery and Physical Properties", J. Can. Petro. Tech., 42(8), 55–61 (2003).

Sury, K.N., "Low Temperature Bitumen Recovery Process", US patent 4 946 597, August 7, (1990).

Sury, K.N., "Low Temperature Bitumen Recovery Process", Canadian Patent 1,302,327, issued June 2 (1992)

Takamura, K. and D. Wallace, "The Physical Chemistry of the Hot Water Process", Can. J. Pet. Tech. 27, 98–105 (1988).

Wallwork, V., "An Investigation of Oil Sand Processability", M.Sc. thesis, University of Alberta, Edmonton, AB (2003).

Wallwork, V., Z. Xu and J. Masliyah, "Processibility of Athabasca Oil Sand Using a Laboratory Hydrotransport Extraction System (LHES)", Can. J. Chem. Eng., 82, 687–695 (2004).

Xu, M., Z. A. Zhou and Z. Xu, "Pre-aeration of Feed", in "Flotation – Encyclopedia of Separation Science", Vol. II, Academic Press, London, UK (2001), pp. 1556–1562.

Zhou, Z. A., Z. Xu and J. H. Masliyah, "Effect of Natural Surfactant Released from Athabasca Oil Sands on Gas Holdup in a Water Column", Can. J. Chem. Eng. 78, 617–624 (2000).

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APPENDEX A7

Published papers:

Zhou, Z., Z. Xu, J.H. Masliyah, T. Kasongo, T. Kizior and D. Cox: “Application of On-Line Visualization to Flotation Systems”, Proceedings-32nd Annual Meeting of The Canadian Mineral Processors (CMP), Paper 7, pp. 119-137, Ottawa18-20, January 2000.

PAPER 7

Application of On-Line Visualization To Flotation Systems

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Key Words: Flotation, bubbles, bubble-particle aggregates, on-line visualization, bitumen

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Application of On-Line Visualization to Flotation Systems

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ABSTRACT

A novel on-line visualization system, previously developed at Syncrude Canada Ltd., has been modified to characterize rising bubbles, particles and particle-bubble aggregates in a flotation process. With this system, the bubble size and rise velocity in a laboratory flotation cell can be determined. The technique allows the loading of solids on bubbles to be visualized, thereby providing an in-depth understanding of sub-processes of flotation. A step-by-step data processing procedure is presented. The applicability of the developed system to mineral flotation and bitumen extraction is discussed. Under batch flotation conditions in a laboratory Denver cell, three main bubble-particle attachment patterns are observed. They are: i) single particles attached to single bubbles, ii) particle aggregates loaded on single bubbles; and iii) a group of particles aggregated with a group of bubbles. The results demonstrate that the on-line visualization system is a powerful tool for understanding and diagnosing flotation processes.

INTRODUCTION

Air (Gas) bubbles are an indispensable component in a flotation system. Both industrial practice and theoretical analysis indicate (Yoon, 1993; Diaz-penafiel and Dobby, 1994) that the size and population of bubbles are two important process parameters in modeling flotation. More recent investigations (Finch, et al., 1999; Gorain, et al., 1997) suggest that for a given flotation system, bubble surface area flux, defined as the air/liquid interfacial area per unit time and unit cross-sectional area of flotation cell, showed a better correlation with the flotation rate constant. As a result, the bubble surface area flux is now being considered as a key parameter to account for the combined effect of bubble size and population in evaluating the performance of flotation machines and modeling flotation processes. However, the success of using bubble surface area flux in flotation process modeling largely depends on how accurate it can be determined or estimated (Finch, et al., 1999).

Efforts have been devoted to developing techniques for on-line characterization of bubbles in a mineral flotation system. The commonly used methods include optical devices, electronic sensors, and photographic techniques. Unfortunately, these methods are not suitable for the study of a complex three-phase slurry system encountered in mineral flotation and bitumen extraction. To gain a better understanding of bubble behavior in a flotation process, a novel on-line visualization system was developed in our laboratory. This on-line visualization system integrates the merit of the similar systems used by Yoon and Luttrell (1986) and by Malysa, et al. (1999). With this system, the behavior of bubbles in a laboratory Denver flotation cell has been visualized and analyzed. The recorded images revealed quite interesting information on bubble behavior and corresponding relationship with flotation performance.

EXPERIMENTAL SET-UP AND PROCEDURES

Experimental Set-Up

An on-line visualization system was developed in this study and a schematic diagram of the setup is shown in Figs. 1a and 1b. The concept born in a large scale on-line visual monitoring system for studying commercial bitumen flotation process (Malysa, et al., 1999) was adopted in the current setup. To allow its use in a laboratory flotation cell, the sampling assembly employed by Yoon and Luttrell (1986) was modified. The sampling probe tube shown in Fig. 1a was made of pyrex glass tube of 8 mm inner diameter. The tube was fused to a 10 × 20 × 85 mm glass cell, where an optical macro-zoom lens was focused on. On the top of the glass cell was an L-shape pyrex tube of 8 mm inner diameter. The free end of the tube was connected to a vacuum line which held reservoir liquid inside the sampling probe assembly. A specially designed Teflon cap was used to block the inlet of the sampling probe tube. Pulling up or pushing down the Teflon cap allowed us to close or open the inlet of the tube at desired periods of the experiments. The gap between the inlet of the tube and the opened cap was maintained at approximately 4 cm to obtain a representative sample of bubbles and bubble-particle aggregates within the flotation cell. The whole assembly was made to fit in a 1-L laboratory Denver flotation cell shown in Fig. 1b. By changing the location of the probe assembly, bubbles at different locations in a flotation cell can be sampled and analyzed.

Experimental Procedures

Before each test, the assembly was immersed in the flotation cell. The clear liquid in the cell was sucked into the assembly to a desired level and held in place under the suction force of a low level vacuum. After conditioning the slurry under given conditions, a predetermined amount of air was introduced. As soon as the Teflon cap was released from the inlet of the sampling probe tube, bubbles with and without loaded solids were sampled under the natural flotation conditions. The moving bubbles, particles and bubble/particle aggregates that entered the probe tube were viewed on line on a TV monitor connected to a CCD-VCR system. The images were recorded with a shutter-speed greater than 1/1000s. A scale was attached to the probe and its sharp image was recorded at the beginning of the test, which served as an internal calibration for the magnified images. The size and rising velocity of bubbles and bubble-particle aggregates were analyzed either on-line during the playback or by transferring the recordings from the video tape to an electronic format using commercial Snappy applications. The later allowed for quantitative analysis.

Image Analysis

A Sony VCR (VHS-SVT-S3100) featuring 60 fields per second recording was used to record the motion of bubbles during flotation. The 60 fields per second was the minimum speed required to record relatively large size bubbles (say, > 2 mm) in two consecutive fields for bubble velocity determination. The recorded images were grabbed and digitized by a Snappy Video Snapshot. The digitized image was then processed using the SigmaScan Pro, an automated image analysis software. The shape factor of the bubble and the Feret bubble diameter, defined as $d_F = (4\ \text{Area}/\pi)^{1/2}$, were calculated using the built-in functions of the software. To determine the rise velocity of a bubble or bubble/particle aggregate, two consecutive frames were analyzed. By tracking the bubbles and aggregates appeared on both frames, the distance traveled by them within the time interval of 1/60 second were measured. This allowed the velocity to be determined.

The applicability of the developed on-line visualization system to a flotation system is illustrated in our preliminary case studies presented below.

CASE STUDIES

1. Minerals Flotation

Single mineral flotation of coal and silica was conducted. During flotation, the aeration rate was kept at 500 mL/min and agitation at 1200 rpm. The solids in the selected size fractions were used, and initial solids content in the pulp was kept at 5% by weight in all flotation tests. Dodecylamine hydrochloride (DAH), purchased from Eastman Kodak, was used as both collector and frother in silica flotation. Methyl isobutyl carbinol (MIBC) from Dow Chemicals was used as frother in coal flotation. DAH and MIBC were used as received, and added to a concentration of 5×10^{-4} and 2×10^{-4} M/L, respectively. Images of bubbles and bubble-solids aggregates in our novel visualization system were recorded during flotation to examine how particles attached to air bubbles and how solids affected bubble sizes.

As a background information, a typical image of bubbles generated in de-ionized water is shown in Fig. 2. Only a few clear bubbles are seen in each frame and the diameter of the bubbles ranges from 1 to 2 mm.

Images of particle-bubble aggregates recorded in coal and silica flotation systems are shown in Fig. 3a-c. Three distinct bubble-particle attachment patterns are observed. Figure 3a shows single coal particles attached to single air bubbles with a significant number of air bubbles unloaded. In Fig. 3b, a few coal particles attached to each air bubble and all the air bubbles were loaded. In silica flotation, a group of silica particles attached to a group of bubbles to form a particle-bubble lump was observed. A selected snapshot of this attachment pattern is shown in Fig. 3c. It should be noted that in the absence of DAH, no silica-bubble attachment was observed and all the air bubbles were free of solids. The presence of bubble-particle lumps in a flotation process suggests that the natural hydrophobic coal or hydrophobized silica particles act as a bridge between the air bubbles. Meanwhile, this bridge also serves as a barrier for bubble–bubble contact and hence their coalescence.

It is evident that for a given number of bubbles, the flotation rate is determined by the number of particles captured per air bubble. Fewer particles captured by an air bubble would result in a lower flotation rate. Clearly, the flotation by the attachment pattern shown in Fig. 3a with a low particle coverage on air bubbles is inefficient. With the attachment pattern shown in Fig. 3c, individual particle attaches to more than one air bubble, decreasing the availability of bubble surfaces for other particles and hence recovery. In terms of froth quality, the attachment pattern shown in Fig. 3c is undesirable because the formation of large bubble-solid aggregates causes inevitable mechanical entrapment of gangue materials. The entrapped gangue particles are often difficult to remove under flotation conditions. To increase bubble loading and minimize the mechanical entrapment of gangue particles, the formation of such large lumps needs to be avoided. Imposing strong mixing to improve hydrodynamic conditions in a flotation cell appears to be a suitable solution to minimize the negative effect. Clearly, the solids-loading pattern given in Fig. 3b is the most favorable for both high flotation recovery and quality froth product.

While increasing solids loading on a bubble is beneficial in terms of full utilization of air bubbles in flotation, the existence of an optimum bubble loading was identified in this work. Depending on the relative size and amount of particles attached to a given bubble, the bubble-particle aggregate may rise or settle. This is clearly seen from the images of two consecutive fields shown in Fig. 4. If the buoyant force of the bubble(s) is smaller than the gravity force of the particles attached to the bubble(s), the bubble-particle aggregate settles. This is the case for the aggregate on the right hand side of the photographs. The estimated settling velocity for this lump is about 3 cm/s. To our best knowledge, this is the first time to directly visualize the settling of particle/bubble aggregates in a running flotation cell. This finding provides a direct experimental evidence to the early speculations that overloading the air bubbles may be undesirable for valuable recovery. An important application of the finding is to account for an optimum range of solids content in the slurry for a maximum flotation recovery, as noted by Finch and Dobby (1990).

Fig. 5 shows the average bubble size measured in flotation reagent solutions without and with solids addition. The results were the average of more than 100 bubbles analyzed for each condition. An increase in bubble size was noted upon the addition of solids, either coal in MIBC solution or silica in amine solution. In the case of coal addition, the average bubble size increased by up to 70%, from about 230 μm to 390 μm. The adsorption of MIBC on hydrophobic coal particles appears to be responsible for the observed increase in average bubble size. It is clear that the technique developed here can be used to clarify the ambiguous effect of solids addition on gas holdups in flotation slurry, an issue debated for some time (Zhou, et al., 1998; Banisi, et al., 1995).

2. Diagnoses of Bitumen Flotation

In Athabasca oil sands processing, both Syncrude Canada Ltd. and Suncor Energy Inc. are using flotation to recover bitumen from oil sands slurry. Flotation was found quite effective for recovering bitumen from high grade oil sands containing more than 10% bitumen. In this case, a bitumen recovery greater than 90% is typical in commercial operations. However, for processing low grade oil sands containing less than 8% bitumen with a relatively high percentage of fine solids and clays, a bitumen recovery less than 50% is not uncommon. In an attempt to identify the major cause(s) for the poor processibility of low grade ores, extensive laboratory tests have been conducted using a batch extraction unit (BEU) (Sanford and Seyer, 1979). However, no conclusive guidelines are available as to which variables, alone or in combination, are critical to bitumen-bubble attachment and hence bitumen recovery. One of the reasons for the slow progress in this area is lack of sensitive techniques to assess the sub-processes in bitumen extraction.

To understand the problems associated with poor bitumen recovery from low-grade oil sands, the bitumen flotation was investigated using the on-line visualization system shown in Fig. 1. A relatively high mixing intensity was employed to facilitate bitumen separation (liberation) from sands. The similar aeration rates to that in the standard BEU test (Sanford and Seyer, 1979) was used in this work. For each test, 450 grams of oil sands were dispersed in 300 mL of hot water (~80 °C) under mechanical agitation at 1800 rpm, and aerated with an airflow rate of 150 mL/min. After continued agitation for 5 min, 650 mL of flood water (~80 °C) was added into the slurry without aeration. *Primary* bitumen froth was collected as a function of time for 10 min. The slurry was then re-aerated at an airflow rate of 50 mL/min to collect the *secondary* bitumen froth for an additional 5 min. All the products, including tailings left in the cell, along with the sampled feed were preserved for bitumen assays, from which bitumen recovery as a function of flotation time was evaluated. The images were recorded during the *primary* bitumen flotation period.

With the high grade oil sands, a *primary* bitumen recovery of about 96% was obtained under natural flotation conditions. A typical snapshot of the images recorded during the flotation is shown in Fig. 6. The load of bubbles with bitumen is evident from the appearance of a dark layer on the air bubbles, compared with the bubbles in de-ionized water shown in Fig. 2. This observation confirms that one of the recovery mechanisms of bitumen is by bitumen engulfing on, and attaching to, air bubbles. A dark brownish color of the bubble (Fig. 6b) is indicative of spreading of thin layer bitumen on the bubble. However, the bubble surface remains macroscopically rugged, suggesting the attachment of bitumen "grains" on the bubbles. This finding appears to contradict to our conventional view of bitumen spreading on bubble in a hot water slurry, which would conform to a smooth spherical shape. The short residence time of bitumen loaded on bubbles in the warm slurry may be one of the reasons for the observed non-spontaneous spreading of bitumen on the bubble surface. It should be noted that in the Denver flotation cell, it only takes a few seconds for bitumen-loaded bubbles to float to the top of the pulp. Over such a short period, the bitumen spreading kinetics dictates the overall non-spreading morphology of bubble-bitumen aggregates. It is clear that the on-line visualization system developed in this study provided us with a unique opportunity to examine the initial stage of bitumen-bubble attachment, a limiting step in bitumen flotation.

To simulate the variations in water chemistry and ore characteristics, bitumen flotation from the high grade oil sands was conducted with the addition of 40 ppm calcium ions and 1 wt.% montmorillonite. In this case, the *primary* recovery was reduced to only about 70%. The image taken during the flotation is shown in Fig. 7. In contrast to those obtained without any additives, the air bubbles here were less colored and some of the bubbles were clear, i.e., not loaded at all. These features indicate a weak attachment of bitumen onto air bubbles. A close examination of Figs. 6 and 7 shows that the bitumen droplets are larger in the slurry without any additives than that with calcium and montmorillonite addition. This observation suggests that the effect of water chemistry and ore characteristics on bitumen coalescence may also be a contributing factor to the reduced bitumen loading on bubbles.

For comparison, the bitumen flotation using low grade oil sands was conducted. In this case, the *primary* flotation recovery was about 70%, similar to that obtained using the high-grade oil sands with added calcium and montmorillonite. The image taken during the primary flotation is shown in Fig. 8. Clearly, the bitumen loading on the air bubbles is essentially the same as those in the slurry of high grade ores with added calcium and montmorillonite. This observation confirms that the poor processability of low-grade oil sands is largely related to the presence of an increased amount of fine clays in the ore and metallic species in process water. The synergetic effect of the two stabilized bitumen droplets and caused insufficient bubble loading, resulting in a low bitumen recovery.

The above case studies demonstrated the value of the developed on-line visualization system in understanding the sub-processes of flotation, diagnosing problems encountered during flotation, and collecting more reliable data for flotation cell design. For example, in flotation cell designs using bubble surface area flux as a key parameter, the developed system provides a unique tool for evaluating the aeration performance of flotation machines. Further work is in progress to quantitatively analyze and correlate the behavior of flotation machines to bubble surface area flux.

CONCLUSIONS

1. A novel on-line visualization system developed in this study has been successfully applied to analyze bubble behavior in a laboratory Denver flotation cell using single mineral and real oil sands samples.
2. Three distinct bubble-particle attachment patterns in a mineral flotation system were observed. They are: i) a single particle attached to a single bubble; ii) a few particles attached to a single bubble; and iii) a group of particles attached to a group of bubbles to form a bubble-particle lump.

3. The settling of the overloaded bubbles with solid particles was observed.
4. The addition of hydrophobic coal to MIBC solution, or silica to amine solution, increased the average bubble size generated in the solution.
5. The poor processibility of low-grade oil sands and the reduced bitumen recovery by calcium and montmorillonite addition to high-grade oil sands are found to be associated with fine size of bitumen droplets and poor bitumen loading on air bubbles.

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REFERECNES

Banisi, S., Finch, J. A., Laplante, A. R. and Weber, M. E., 1995, "Effect of solid partciels on gas holdup in flotation columns", *Chem. Eng. Sci.*, Vol. 50, pp. 2329-2342.

Diaz-penafiel, P. and Dobby, G. S., 1994, "Kinetic studies in flotation columns: bubble size effect", *Minerals Eng.*, Vol. 7, pp. 465-478.

Finch, J. A., Gomez, C. O., Hardie, C., Leichtle, G., Filippone, R. and Leroux, D., 1999, "Bubble surface area flux: A parameter to characterize flotation cells", Proceedings – 31st Annual Meeting of the Canadian Mineral Processors, paper 13, pp. 199-209.

Finch, J. A. and Dobby, G. S., 1990, Column Flotation, Pergamon Press.

Gorain, B. K., Franzidis, J. P. and Manlapig, E. V., 1997, "Studies of impeller type, impeller speed and air flow rate in an industrial scale flotation cell, Part 4: Effect of bubble surface area flux on flotation performance", *Minerals Engineering*, Vol. 10, No. 4, pp. 367-379.

Malysa, K., Ng, S., Cymbalisty, L., Czarnecki, J. and Masliyah, J., 1999, "A method of visualization and characterization of aggregate flow inside a separation vessel", *Inter. J. Miner. Process.*, Vol. 55, pp. 171-202.

Sanford, E. C. and Seyer, F. A., 1979, "Processibility of Athabasca tar sand using a batch extraction unit: The role of NaOH", *CIM Bulletin*, Vol. 72, pp. 164-169 (March, 1979).

Yoon, R. H. and Luttrell, G. H., 1986, "The effect of bubble size on the fine coal flotation", *Coal Preparation*, Vol. 2, pp. 179-192.

Yoon, R. H., 1993, "Microbubble flotation", *Minerals Engineering*, Vol. 6, pp. 619-630.

Zhou, Z. A., Xu, Z. and Finch, J. A., 1998, "Effect of surface properties of fine particles on dynamic bubble formation in gas-supersaturated systems", *Ind. Eng. Chem. Res.*, Vol. 37, pp. 1998-2004.

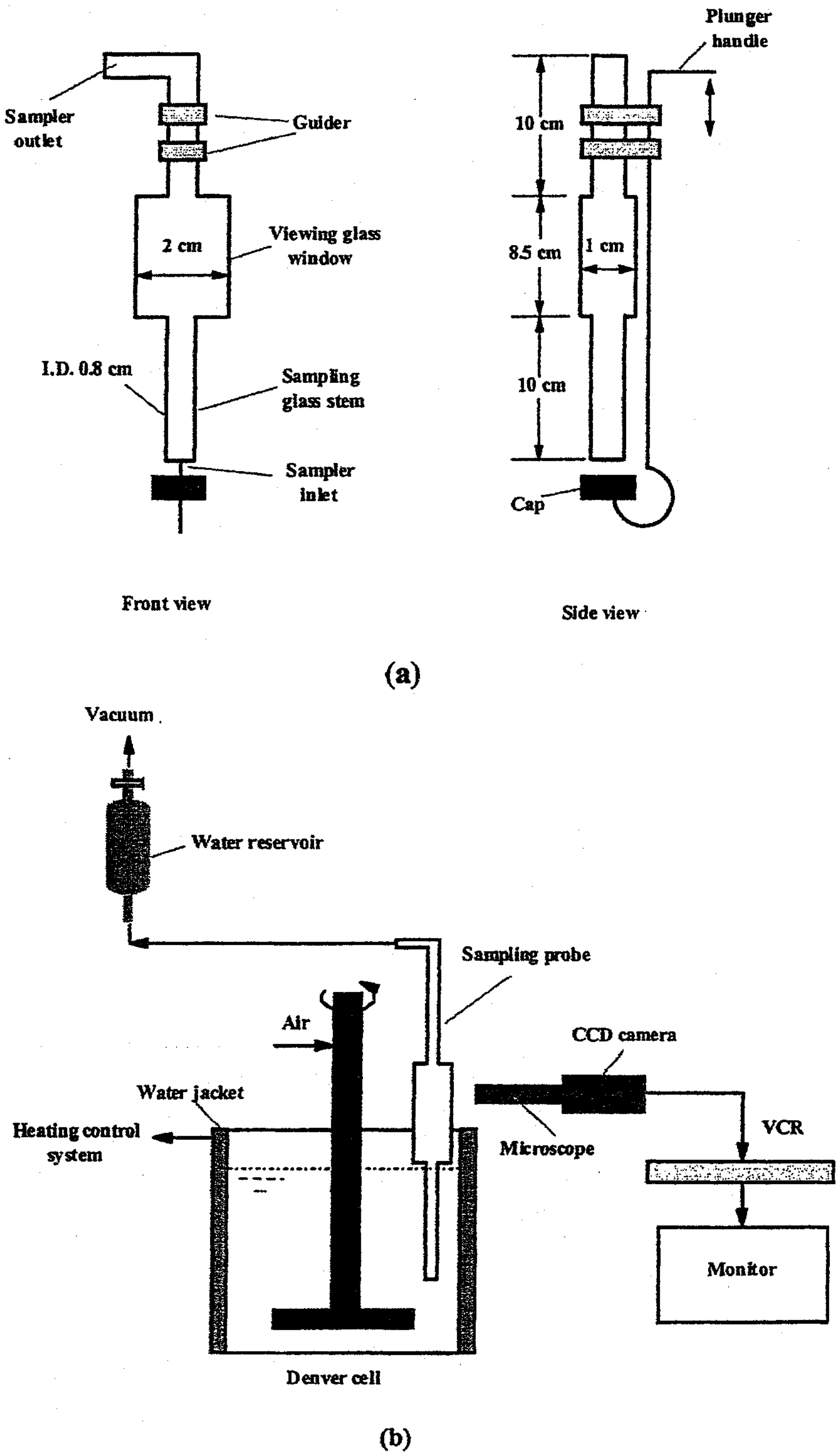

Figure 1. **Schematic of a visualization probe system developed in this study**

a. Layout of the system

b. Design of a sampling probe

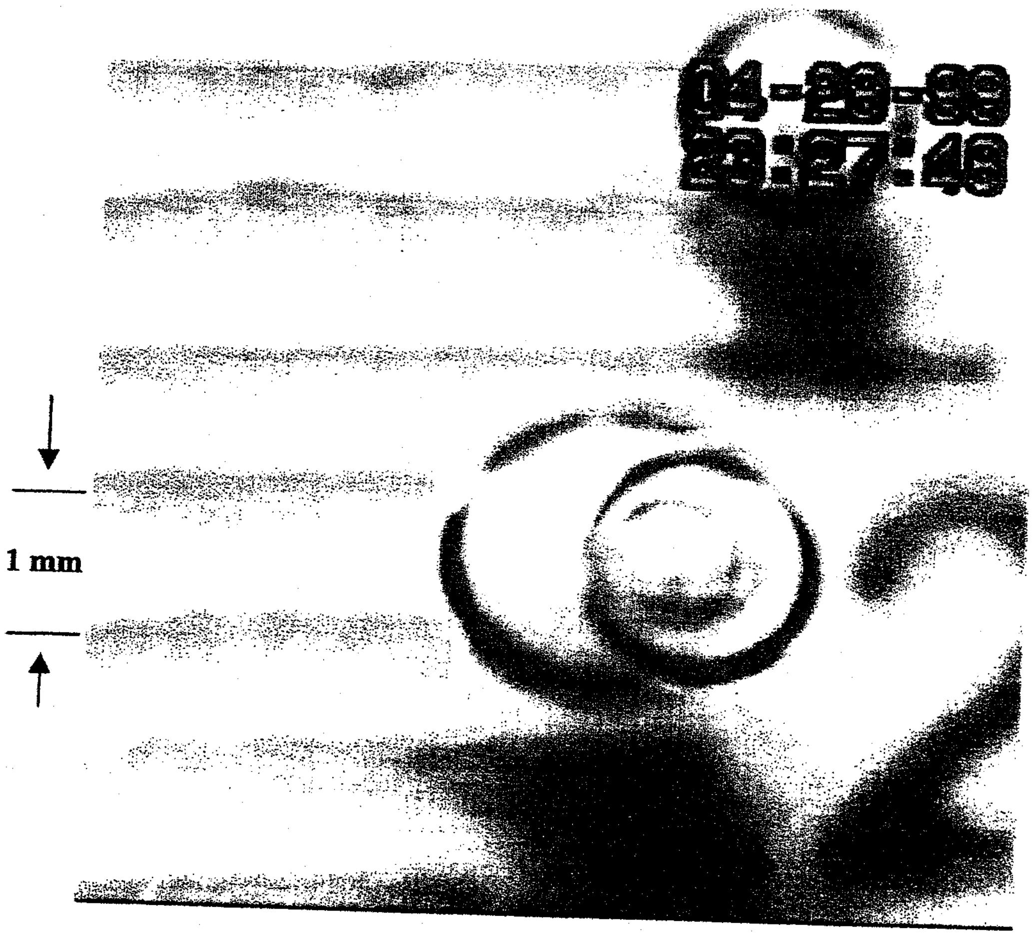

Figure 2. **Bubbles in de-ionized water at aeration rate of 150 ml/min, agitation speed of 1800 rpm and room temperature**

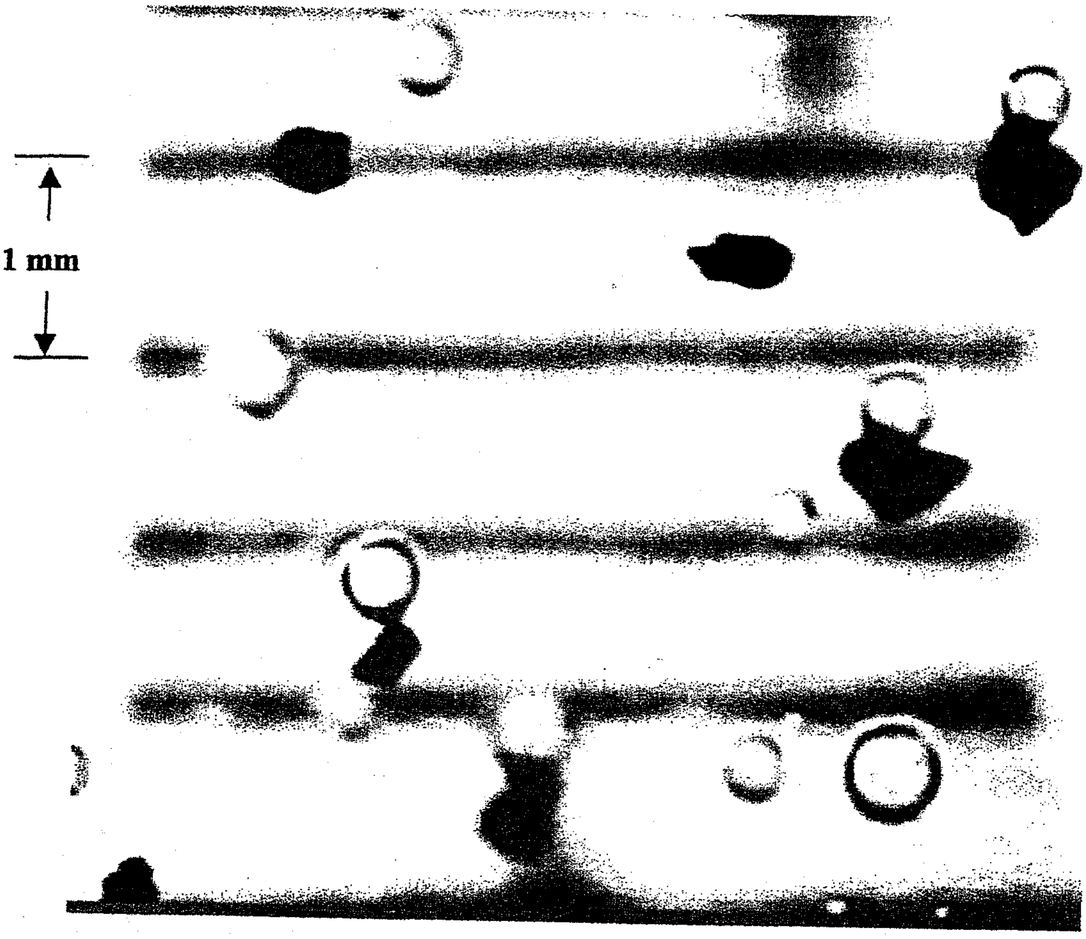

Figure 3a. **Attachment pattern 1: single particle attached to single air bubble (coal particle size: -300+210 μm)**

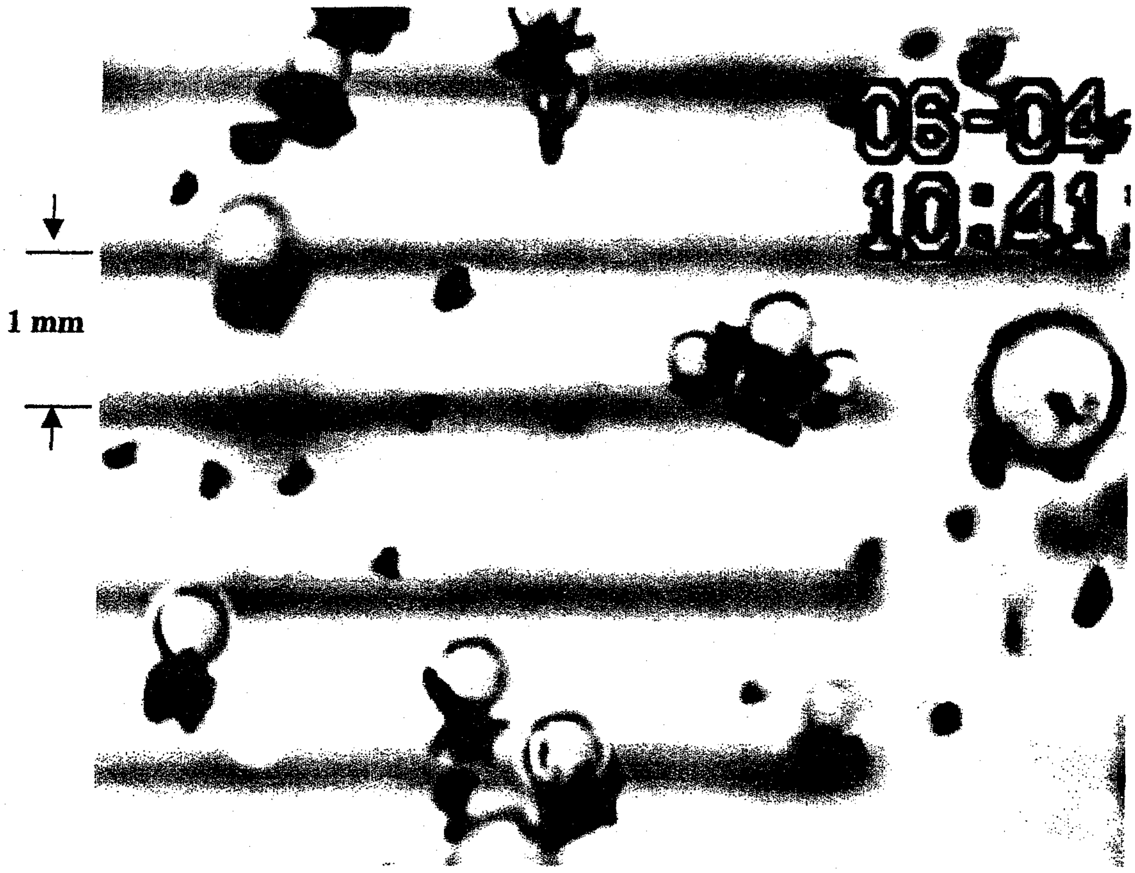

Figure 3b. Attachment pattern 2: few particles attached to single bubble (coal particle size: -210+150 μm)

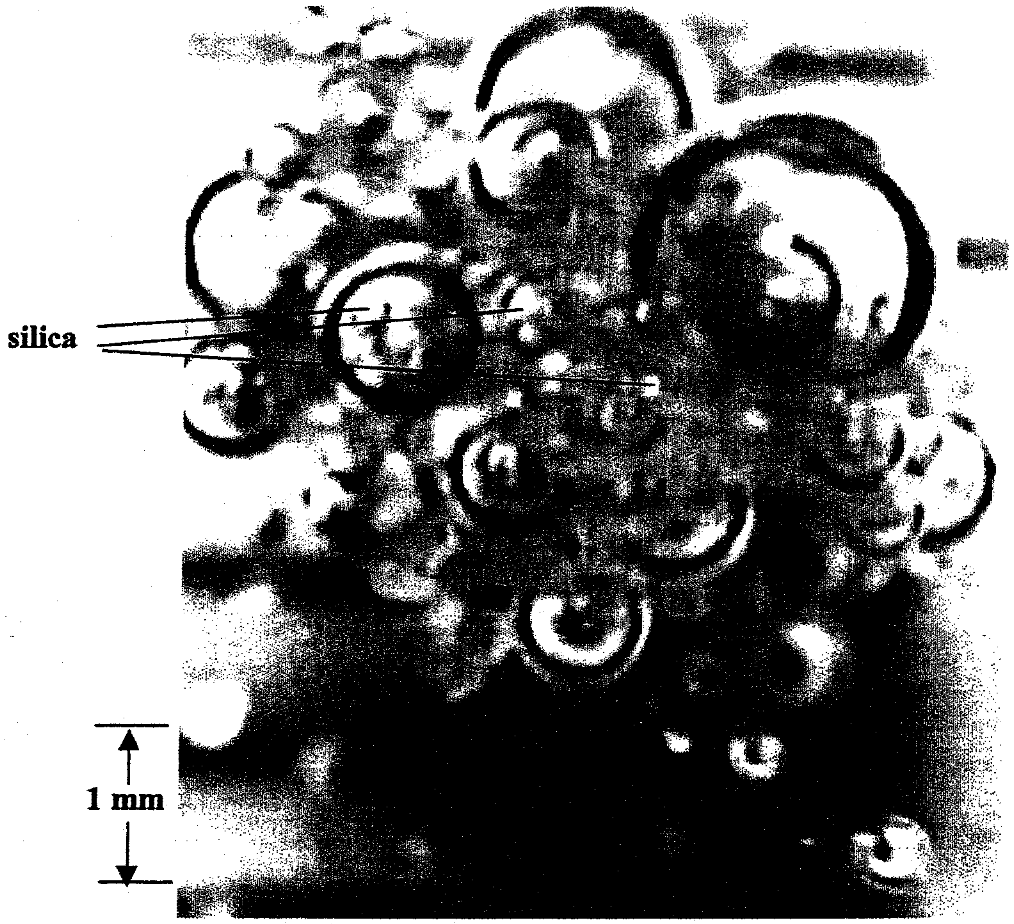

Figure 3c. Attachment pattern 3: a group of particles attached to a group of bubbles (silica particle size: -210+150 μm)

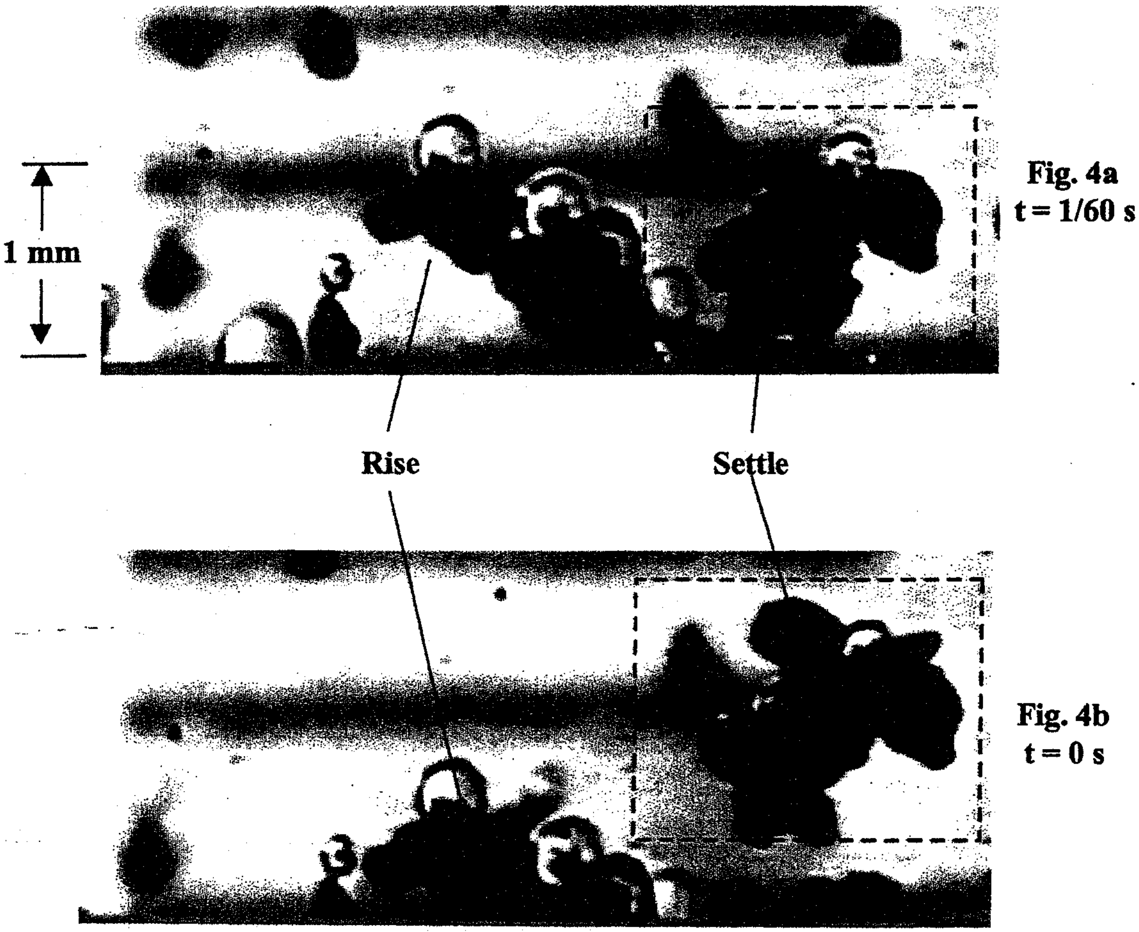

Figure 4. Effect of particle loading on the rise velocity of bubble-particle aggregates (coal particle size: -300+210 μm)

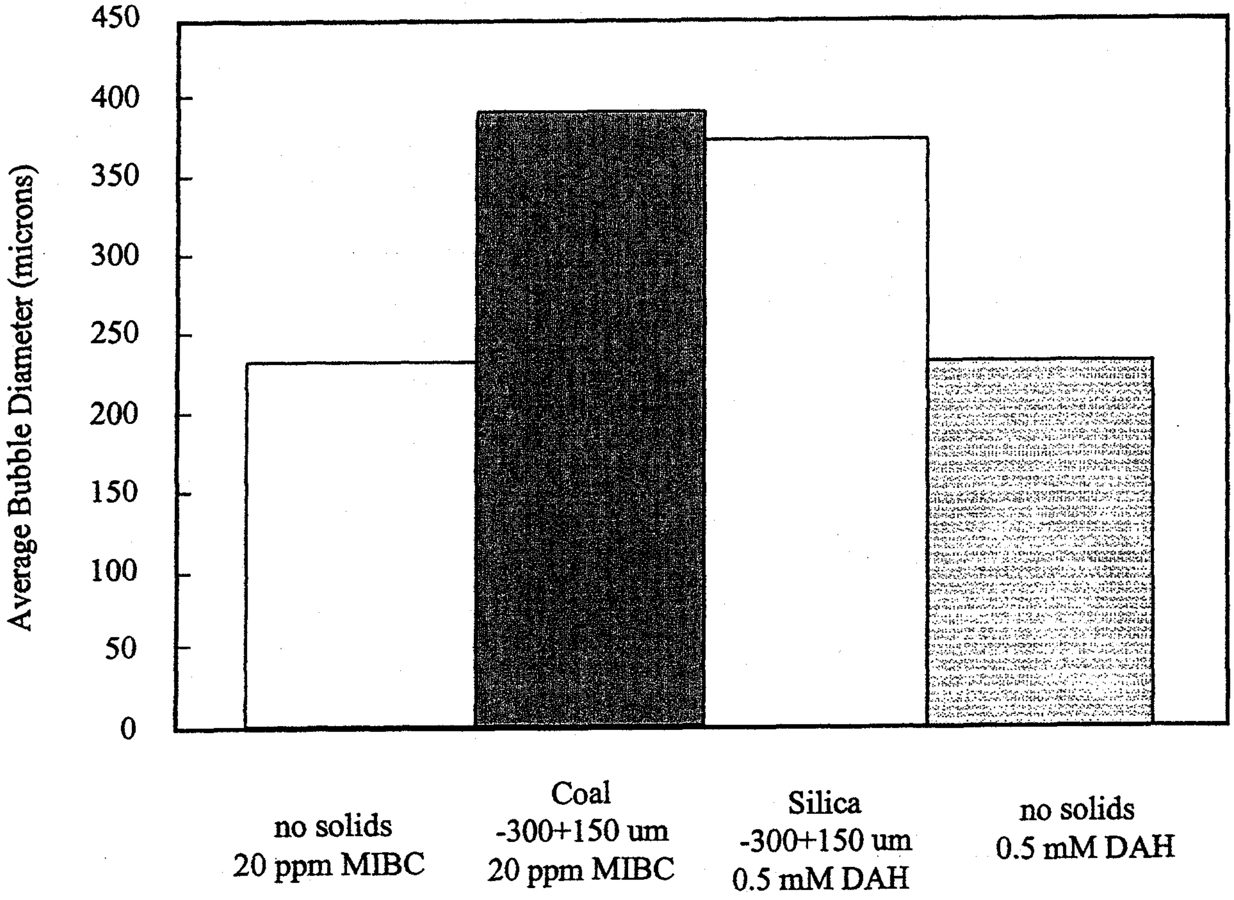

Figure 5. **Effect of solids addition on average air bubble size**

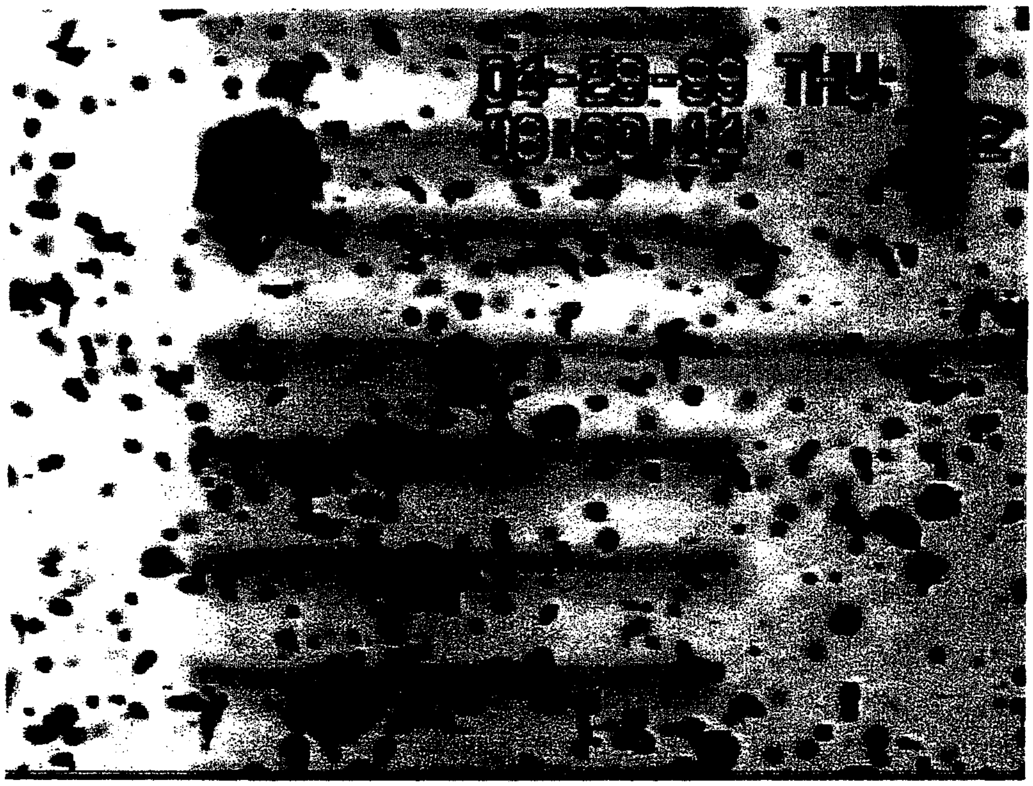

Figure 6a. Bitumen flotation from high grade oil sands under natural conditions at 76°C

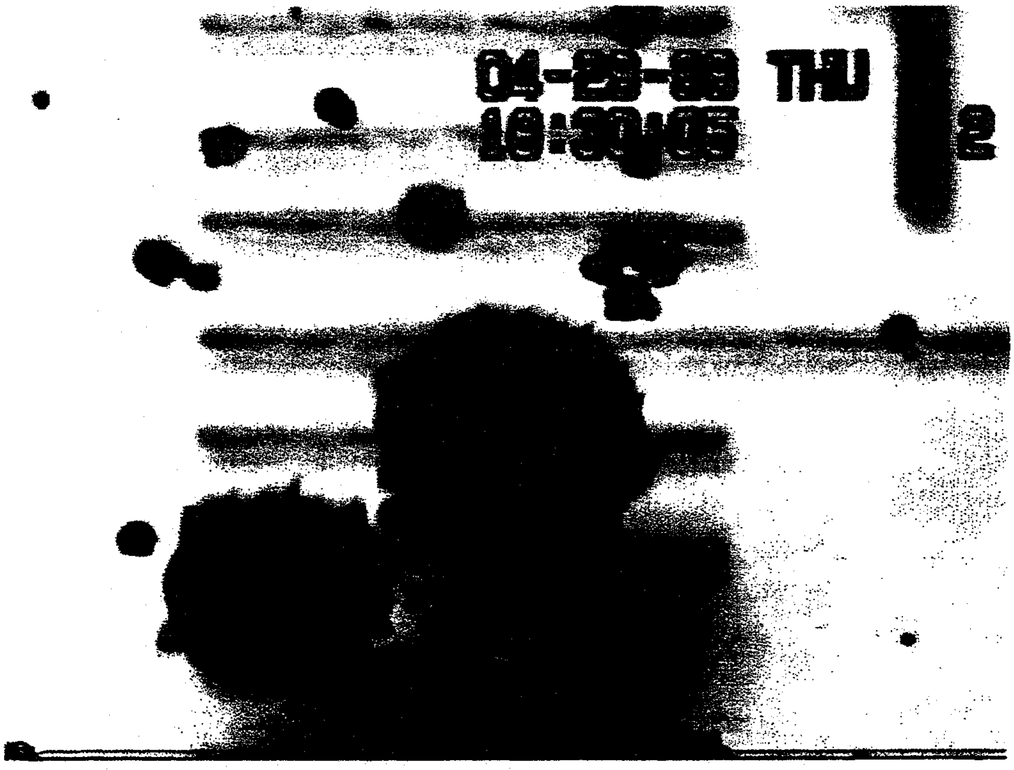

Figure 6b. Bitumen loading on air bubbles, images taken during flotation of high grade oil sands under natural conditions at 76°C

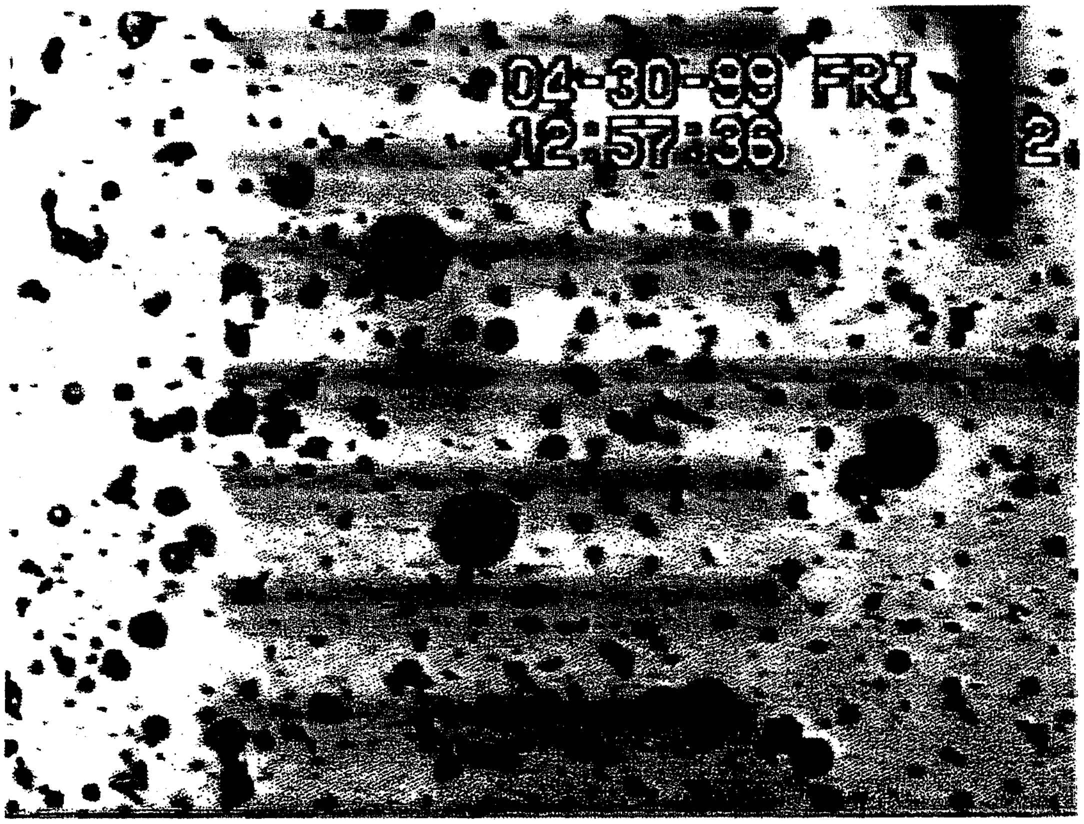

Figure 7. Bitumen flotation from high grade oil sands with the addition of 40 ppm calcium and 1wt.% montmorillonite at 76°C

Figure 8. Bitumen flotation from low grade oil sands under natural conditions at 76°C