October 2015

Fundamentals of Electro-Flotation and Electrophoresis and Applications in Oil Sand Tailings Management

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A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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FUNDAMENTALS OF ELECTRO-FLOTATION AND ELECTROPHORESIS AND APPLICATIONS IN OIL SAND TAILINGS MANAGEMENT

(Thesis Format: Integrated-Article)

By

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Graduate Program
in Engineering Science

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A thesis submitted in partial fulfilment of the requirements for

the degree of Doctor of Philosophy

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ABSTRACT

This thesis addresses two challenges facing the management of mature fine tailings (MFT) from oil sand processing. The first challenge is the high concentration of residual bitumen in tailings ponds, which poses a hazard to aquatic biota and impact to the environment. A laboratory scale study is carried out to assess the suitability of electro-flotation (EF) for removal of bitumen from oil sand tailings slurry. The results of the study confirm that EF is effective to reduce bitumen contents of tailings slurry. At a current density 150 A/m², the bitumen concentration is reduced from 106.8 mg/L to less than 10 mg/L within 90 minutes. The electrolysis voltage has direct impact to the operating cost of an EF system, hence an electrochemical model is developed to predict the total electrolysis voltage required for an EF cell. Good agreement is found between the simulation results and experimental data from both this study and the literature. Hence the model derived can be used to predict the total electrolysis voltage required for an EF cell and to optimize operating conditions of an EF cell to reduce the operating cost. The performance of EF is strongly influenced by the size of O₂ and H₂ bubbles. Therefore, in this study the bubble sizes are measured in a lab scale EF cell using a high-speed camera. The mean bubble size is found to vary in the range of 32.7–68.6 μm under different operating conditions. This study shows that the electrode material, current density, water pH, ionic strength, and frother (Tennafroth 250) concentration are important factors in controlling the bubble size. Furthermore, four mathematical distributions (normal, log-normal, Weibull and gamma distributions) are fitted to the experimental data, among which the log-normal distribution is found to be the best fit based on the lower Anderson-Darling (AD) value.
The second major challenge is to thicken and consolidate the MFT for water recycling and land reclamation. The suitability of electrokinetic (EK) sedimentation to accelerate sedimentation of MFT is investigated in this study. Based on the experimental data, an electric field intensity of 150V/m along with an initial tailings solid concentration of no more than 5% are the optimum operating condition for EK sedimentation of MFT, in terms of reducing the overall sedimentation time and increasing the final solid concentration. The results show that the current density of EK sedimentation for MFT should not be more than 20 A/m² to control the bubble effect and reduce power consumption.

**Keywords:** Electro-flotation, Electrophoresis, Electrochemistry, Sedimentation, Oil sand tailings, Electric Field, Electrode, Electrolysis, Bitumen, ANOVA.
This thesis was written in accordance with the guidelines and regulations for a manuscript format stipulated by the Faculty of Graduate Studies at the University of Western Ontario. The candidate developed all analytical modeling; and paper preparation under a close guidance and supervision of Dr. J.Q. Shang. The following sections of the thesis will be submitted to scientific journals with co-authors as indicated.

Chapter 2: A review of fundamentals and applications of electro-flotation and electrophoresis

A version of this chapter has been submitted to the Journal of Environmental Technology & Innovation, Elsevier in 2015.

The contributions of the co-authors are:

Alam, R.: wrote the draft and final version of the paper.

Shang, J. Q.: made major revision of the paper.

Chapter 3: Electrochemical model of electro-flotation

A version of this chapter has been submitted to the Journal of Water Process Engineering, Elsevier in 2015.

The contributions of the co-authors are:
Alam, R.: analysed and interpreted the results of the laboratory study, conducted the modelling, and wrote the draft and final version of the paper

Shang, J. Q.: contributed advice on modelling and made major revision of the paper.

Chapter 4: Bubble size distribution in laboratory scale electro-flotation study

A version of this chapter has been submitted to the International Journal of Mineral Processing, Elsevier in 2015.

The contributions of the co-authors are:

Alam, R.: carried out experiments and analysed the results of the laboratory study and wrote the draft and final version of the paper

Shang, J. Q.: made major revision of the paper.

Khan, A. H.: helped to carry out the experiments.

Chapter 5: Removal of bitumen from mature oil sands tailings slurries by electro-flotation

A version of this chapter has been submitted to the Journal of Mine Water and the Environment, Springer in 2015.

The contributions of the co-authors are:
Alam, R.: carried out experiments, analysed and interpreted the results of the laboratory study, conducted the modelling, and wrote the draft and final version of the paper.

Shang, J. Q.: contributed advice on modelling and made major revision of the paper.

Chapter 6: Electrophoresis and its applications in oil sand tailings management

A version of this chapter has been submitted to the Journal of Environmental Management, Elsevier in 2015.

The contributions of the co-authors are:

Alam, R.: conducted the research, analysed and interpreted the results of the laboratory study, conducted the modelling, and wrote the draft and final version of the paper.

Shang, J. Q.: contributed advice on modelling and made major revision of the paper.

Islam, S.: helped to carry out the experiments
ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr. Julie Q. Shang, for her guidance, encouragement, enthusiasm and motivation throughout my PhD study. Working in her group offered me the opportunity to spend more than four stimulating years working on an attractive area of research.

This research was made possible by the support of ESSO URA, NSERC, DST Consulting Engineers and COSIA.

I would also like to thank Mr. Adnan Hossain Khan, Mr. Shriful Islam, Mr. Xinwei Chen, Mr. Puneet Verma, and Mr. Yu Guo for their help during my research. I am grateful to Mr. Tim Stephens, Mr. Erol Tas, Ms. Melodie Richards and Ms. Caitlin Marshall for their assistance and co-operation during the laboratory tests. I am very grateful to Professor Ajay Ray for giving me the permission to use Fourier transform infrared spectroscopy (FTIR) in Western Advanced Analysis and Materials Testing Laboratory. I am also thankful to Dr. Mark Biesinger for helping me on X-ray Photoelectron Spectroscopy (XPS) analysis. I would like to extend my gratitude to the Faculty and Staff of the Department of Civil and Environmental Engineering, especially to Ms. Whitney Barrett, Ms. Stephanie Lawrence, and Ms. Cynthia Quintus.

I am especially grateful to my family for supporting and encouraging me during my studies.
DEDICATION

Dedicated to the ultimate sources of love and inspiration

My father Tarek-Ul-Alam & my mother Rukhsana Alam

My wife Farhana Jesmin

My sons Rayyan and Rafan

And my younger brother Saiful Alam

Without whom this thesis would not have been possible
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**REMOVAL OF BITUMEN FROM MATURE OIL SANDS TAILINGS**

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<tr>
<td>((i_0)_a)</td>
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<td>((i_0)_c)</td>
<td>Standard current densities at the cathode (A/m²)</td>
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<td>(A)</td>
<td>Surface area of electrode (m²)</td>
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<td>(A_{11})</td>
<td>Hamaker constants</td>
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<td>(a_a)</td>
<td>Constant of Tafel equation at the anode</td>
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<td>(b_a)</td>
<td>Tafel slope of Tafel equation at anode</td>
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<td>(b_c)</td>
<td>Tafel slope of Tafel equation at cathode</td>
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<td>(C)</td>
<td>Final concentrations of bitumen (mg/L)</td>
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<td>(C_0)</td>
<td>Initial concentrations of bitumen (mg/L)</td>
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<tr>
<td>(C_{H^+}</td>
<td>_{x=0})</td>
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<tr>
<td>(C_{H1^+}</td>
<td>_{x=0})</td>
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<tr>
<td>(C_{m}(x))</td>
<td>Concentration of species m at distance x, (mol/L)</td>
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<td>(d)</td>
<td>Distance between the anode and cathode (m)</td>
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<tr>
<td>(d_{b/H})</td>
<td>Mean bubble dia of H₂ (m)</td>
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<td>(d_{b/O})</td>
<td>Mean bubble dia of O₂ (m)</td>
</tr>
<tr>
<td>(D_{H^+})</td>
<td>Diffusion coefficient of the [H⁺] (m²/s)</td>
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<td>(D_m)</td>
<td>Diffusion coefficient of species m, (m²/s)</td>
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</table>
\(d_O\) Mean bubble dia of \(O_2\) (m)

\(D_{OH^-}\) Diffusion coefficient of the \([OH^-]\)

\(E\) Electric field intensity (V/m)

\(E_{cell}\) Electrolysis voltage (V)

\(E_{eq}\) Equilibrium potential difference for water split (V)

\(F\) Faraday’s constant (96,500 C/mol of electrons)

\(f_f\) Fraction of free particle

\(f_H\) Fraction of total \(H_2\) transformed into bubbles.

\(f_O\) Fraction of total \(O_2\) transformed into bubbles

\(f_O\) Fraction of total \(O_2\) transformed into bubbles.

\(g\) Gravitational acceleration (m/s\(^2\))

\(h\) Thickness of bubble layer (m)

\(i\) Local current (A)

\(j\) Current density (A/m\(^2\))

\(J_{H^+}\) Flux of \([H^+]\) (mol/m\(^2\) s\(^1\))

\(J_{OH^-}\) Flux of \([OH^-]\) (mol/m\(^2\) s\(^1\))

\(K\) Flotation rate constant (min\(^{-1}\))

\(K_1\) Particle-bubble attachment rate constant

\(k_b\) Boltzmann constant

\(n\) Porosity of the suspension

\(N_{bT}\) Total number of bubbles present in the flotation cell per sec

\(n_H\) Electrons transfer number of \(H_2\)

\(N_H\) Total number of hydrogen bubbles generate in an EF cell per unit time
<table>
<thead>
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<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>( n_0 )</td>
<td>Electrons transfer number of ( O_2 )</td>
</tr>
<tr>
<td>( N_0 )</td>
<td>Total number of oxygen bubbles generate in an EF cell per unit time</td>
</tr>
<tr>
<td>( P_a )</td>
<td>Probabilities of particle–bubble adhesion</td>
</tr>
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<td>Probabilities of particle–bubble stabilisation</td>
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<td>( Q_H )</td>
<td>Generating rates of ( H_2 ) (L/sec)</td>
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<tr>
<td>( Q_O )</td>
<td>Generating rates of ( O_2 ) (L/sec)</td>
</tr>
<tr>
<td>( r )</td>
<td>Coefficient of sedimentation</td>
</tr>
<tr>
<td>( R )</td>
<td>Ideal gas law constant (8.314 J/K mol)</td>
</tr>
<tr>
<td>( R(%) )</td>
<td>Bitumen removal rate</td>
</tr>
<tr>
<td>( Re_b )</td>
<td>Bubble Reynolds number</td>
</tr>
<tr>
<td>( r_{ek} )</td>
<td>Sedimentation coefficient at hindered settling stage</td>
</tr>
<tr>
<td>( R_x )</td>
<td>Modified electrochemical cell resistance</td>
</tr>
<tr>
<td>( t )</td>
<td>Time (min)</td>
</tr>
<tr>
<td>( T )</td>
<td>Absolute temperature (K)</td>
</tr>
<tr>
<td>( t_{ind} )</td>
<td>Induction time (min)</td>
</tr>
<tr>
<td>( t_m )</td>
<td>Transport number of species ( m )</td>
</tr>
<tr>
<td>( U )</td>
<td>Suspension settling velocity (m/s)</td>
</tr>
<tr>
<td>( u )</td>
<td>Particle settling velocity (m/s)</td>
</tr>
<tr>
<td>( U_b )</td>
<td>Bubble rise velocity (m/s)</td>
</tr>
<tr>
<td>( u_{ek} )</td>
<td>Particles velocity induced by electrokinetics (m/s)</td>
</tr>
<tr>
<td>( u_f )</td>
<td>Bubble-particle aggregate velocity acting upward in the EK</td>
</tr>
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</table>
\( u_g \)  
Particle settling velocity due to the gravity (m/s)

\( v(x) \)  
Convective velocity of water flow in the current direction at distance \( x \),

\( V_0 \)  
Molar volume of gases at the normal state (22.4L/mol)

\( Z_1 \)  
Coefficient related to the particle–bubble collision frequency

\( \alpha_a \)  
Anodic transfer coefficients

\( \alpha_c \)  
Cathodic transfer coefficients

\( \beta \)  
A factor which represents an average velocity of all particles

\( \beta_{h-ek} \)  
Factor that relates the particle’s terminal velocity and suspensions

\( \delta_a \)  
Diffusion layer thickness at the anode (m)

\( \delta_c \)  
Diffusion layer thickness at cathode (m)

\( \varepsilon \)  
Volume fraction of bubbles

\( \varepsilon_w \)  
Permittivity of water (F/m)

\( \zeta \)  
Zeta potential (V)

\( \eta_{a,a} \)  
Anode activation overpotential (V)

\( \eta_{a,c} \)  
Anode concentration overpotential (V)

\( \eta_{a,p} \)  
Anode passive overpotential (V)

\( \eta_{c,a} \)  
Cathode activation overpotential (V)

\( \eta_{c,c} \)  
Cathode concentration overpotential (V)

\( \eta_{\text{ohm}} \)  
Ohmic overpotential (V)

\( \theta \)  
Contact angle in degree

\( \kappa \)  
Debye–Hückel parameter

\( \mu \)  
Viscosity of water (N-s/m²)

\( \rho \)  
Electrical resistivity (Ω·m)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>(\rho_p)</td>
<td>Mass density of the particles (kg/m(^3))</td>
</tr>
<tr>
<td>(\rho_w)</td>
<td>Mass density of water (kg/m(^3))</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Electrical conductivity (S/m)</td>
</tr>
<tr>
<td>(\sigma_x)</td>
<td>Electrical conductivity of the gas–liquid dispersion (S/m)</td>
</tr>
<tr>
<td>(\theta)</td>
<td>Fraction of electrode covered by bubbles</td>
</tr>
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CHAPTER 1

INTRODUCTION

1 Background

The oil sands in northern Alberta, Canada, have a reserve of 174 billion barrels of bitumen (Alberta Energy and Utilities Board 2005) of which 1 million barrels (National Energy Board 2006) is extracted every day. The Canadian oil sands industry withdraws an average of 3 barrels of freshwater for every barrel of oil produced (Allen, 2008). The resulting process water of the oil sands mining operation (oil sand tailings) is discharged in large tailings ponds. Allen (2008) has identified some target pollutants in the tailings ponds’ water, which should be reduced to an allowable level so that the tailings can be used directly in the reclamation process. Residual bitumen, one of the target pollutants poses a hazard to aquatic biota, and its biodegradation could be a source of Naphthenic Acid (Quagraine et al. 2005). Bitumen would disturb aquatic communities in reclamation ponds, and contribute to the fouling of advanced treatment technologies. Bitumen concentrations (measured as oil and grease) in tailings ponds water have been at least 2.5 to 9 fold higher than the EPEA maximum discharge limit of 10 mg/L, thus up to 90% removal may be required (Allen, 2008).

Electro-flotation (EF) is an electrochemical technology that is effective for separation of oil from oil-water emulsions (Matis and Peleka, 2010, Hosny, 1996, Mansour and Chalbi, 2006, Ibrahim et al. 2001, Vasibenko et al, 1973; Balmer and Foulds 1986; Il’in 2002; Il’in
and Sedashova 1999). Therefore, this research is initiated to assess the feasibility of EF for removal of bitumen from oil sand tailings slurry. The operating cost is one of the primary concerns for the performance of an EF system. Operating cost depends on the power consumption that is strongly reliant on the electrolysis voltage. Therefore, this research also focuses on to develop an electro-chemical model to predict the electrolysis voltage under desired operating conditions. The flotation kinetics of any flotation system including EF is strongly influenced by the size of the bubbles (Ahmed and Jameson, 1985). However the uncertainty in influences of variables on bubble size has made it difficult to effectively design efficient EF systems (Sarker, 2010). Therefore this research also investigates the size of hydrogen and oxygen bubbles produced under different operating conditions.

Another major challenge of the oil sands tailings management is to thicken and consolidate the mature fine tailings to reduce the dedicated disposal areas (DDAS) (Farkish, 2013). Whenever, the end products of the oil sands mining operation are pumped into large tailings ponds, the coarse solids, mostly sands, settle down quickly (Alam et al, 2014). However, fine solids, remain suspended in tailings ponds, which take years to consolidate and are known as mature fine tailings (MFT) (Johnson et al., 1993). The MFT are a mixture of residual bitumen, sand, silt, and clay particles (Alam et al, 2014). Due to the poor water release ability, low hydraulic conductivity and low strength of the MFT, dewatering under natural conditions is not realistic (Mikula et al., 1996). Currently more than 170 km$^2$ of Alberta’s lands are covered by tailings ponds, and expected to occupy an area of 250 km$^2$ by 2020, (Government of Alberta, 2012), which causes serious environmental concerns, such as impacts on public health, land use, water supply and air quality (Farkish, 2013). Electrokinetic (EK) thickening is a potential option to enhance the thickening process of
fine oil sand tailings (Alam et al, 2014). Electrokinetics has been studied extensively in geotechnical engineering applications (e.g. Fourie et al., 2007, Mohamedelhassan, 2008; Rittirong et al., 2008, Shang et al., 2009, Islam, 2014), including consolidation of soft clays, dewatering of mine tailings, strengthening of marine sediments and so on (Alam et al, 2014). The research on dewatering of oil sands MFTs using EK technology has been reported (Guo and Shang, 2014), which focused on the assessment of the effectiveness and efficiency of EK dewatering of MFT (Alam et al, 2014). Therefore, this research is initiated on the electrokinetic sedimentation of the MFT to improve the settling time as well as to increase the final solid concentration.

Both electrokinetic sedimentation and electroflotation have potential applications in oil sand tailings management. These two technologies can be applied in two stages. In stage one, electrokinetic sedimentation can be used to recover process water by solid–liquid separation and enhance the free settling velocities of tailings. In stage two, the electroflotation can be introduced to remove residual bitumen from the process waters (recovered in stage one) so that it can be safely recycled for oil production or can be discharged into Athabasca river. The thickened sludge of stage one might need further treatment for dewatering by electro-osmosis.
1.1 Research Objectives

The objective of this research is to study the fundamentals and feasibility of electro-flotation (EF) and electrokinetic (EK) sedimentation in oil sand tailings management. The specific goals of the study include:

I. To critically review the fundamental principles of EF, its limitations, areas that need further improvement and future prospects.

II. To establish the theoretical models regarding the electrolysis voltage required in an EF process and to verify the simulation results by comparing with experimental data from this study as well as data obtained from the literature.

III. To investigate the size of hydrogen and oxygen bubbles produced from Stainless steel (SS 316) and Ti-IrO₂ electrodes as a function of current density, pH, electrode geometries, KNO₃ concentration and frother concentration.

IV. To study the performance of EF from a laboratory scale electro flotation cell for removal of bitumen from oil sand tailings slurry and to study the flotation performance as affected by operating parameters (Current density, pH, bitumen concentration and salt dosage for conductivity adjustment).

V. To investigate EK sedimentation for thickening of mature fine tailings, with focus on improving the settling time and increasing solid content. The influencing factors, including the initial solid concentration of the MFT suspension, electric field intensity, water pH, and the use of an optimized coagulant FeCl₃, are studied in detail based on experimental results and statistical analyses.
1.2 Thesis Outline and Scope

The thesis consists of seven chapters, the contents of which are as follows:

Chapter 1 introduces the engineering background of the thesis, defines the objectives and goals of the research, and states the original contributions of the study.

Chapter 2 provides a comprehensive literature review on fundamentals and applications electro-flotation and electrokinetic sedimentation.

Chapter 3 presents an analytical model to simulate the electrolysis voltage of an EF cell. The model was developed based on the experimental results of EF cell.

Chapter 4 presents the influence of current density, pH, ionic strength of the electrolyte, electrode materials, and frother concentration on both hydrogen and oxygen bubble size distributions in an EF cell.

Chapter 5 presents an experimental design of laboratory scale EF tests, which was carried out to assess the suitability of EF for removal of bitumen from mature oil sands tailings slurries.

Chapter 6 presents an experimental design of laboratory scale EK sedimentation tests which was carried out to assess the feasibility of EK sedimentation for quick settlement of mature fine tailings.

Chapter 7 summarizes the key aspects and draws conclusions of the research, and makes recommendations for further researches.
Chapter 2, 3, 4, 5 and 6 are presented as the manuscript format for different but related topics. Since the contents of the chapters are in preparation for publications in technical journals, there might be overlap in the introduction and experimental sections in individual chapters.

1.3 Original Contribution

The original contributions include:

I. Demonstration of the effect of bubbles between electrodes on electrolysis voltage of EF and presentation of an analytical model based on the Nernst equation, Tafel equation, Fick’s model, and Ohm’s law to calculate the total required electrolysis voltage for an EF cell under different operating conditions.

II. Presentation of a comprehensive laboratory technique to investigate the size of hydrogen and oxygen bubbles produced under different operating conditions. The study also provides vital information regarding the mathematical distribution of bubble sizes.

III. Evaluation of the suitability of EF for removal of bitumen (measured as oil and grease) from oil sand tailings slurry. A first order kinetic model is developed to predict the performance of EF in terms of removal of bitumen (%) from tailings slurry under a specific operating condition. A framework is developed for the mining company to identify the key operational parameters of EF for removal of bitumen from tailings slurry.
IV. Design of an experimental program for thickening of mature oil sand tailings slurry. An analytical model is developed to evaluate the effect of bubbles on the free settling velocity of the settling particles in EK sedimentation. Second order polynomial equations are presented to correlate final solid concentration (%) and free settling velocity (cm/hr) with two most important factors of the EK sedimentation, i.e. the initial solid concentration and electric field intensity. Although the laboratory scale study is being carried out using site specific materials, the principles of the design and implementation can be applied for thickening of tailings on mine sites.
1.4 References


Il’in, V. I., Kolesnikov, V. A., Parshina, Y. I. 2002. Purification of highly concentrated industrial sewage from the porcelain and faience industry by the electric flotation method. Glass Ceram. 59(7–8), 242–244.


CHAPTER 2

A REVIEW OF FUNDAMENTALS AND APPLICATIONS OF ELECTRO-FLOTATION AND ELECTROPHORESIS

2 Electro-flotation

Flotation is defined as a unit operation for solid-liquid separation by introducing fine gas bubbles into the liquid phase. The bubbles attach to the particle surface and the buoyant force of the bubble-particle aggregate is adequate to cause the particle to rise to the surface (Metcalf and Eddy, 1991). Once the particles are floated to the surface, they can be collected by skimming operation (Wang et al, 2007). This technology is generally used in industrial and environmental applications, such as metal-slurry separation in the mining industry (Ahmed and Jameson, 1985; Ketkar et al, 1992) and waste-water treatment (Zabel, 1985).

Gas bubbles can be produced through many methods, for example, dissolved air-flotation, electrostatic spraying of air, and electrolysis, which is the principle of electro-flotation (Burns, 1997). Conventional flotation cells generate large bubbles, ranging in size from 600 to 2000 μm (Wills, 1997) while some spargers can produce medium bubble sizes from 100 to 600 μm (Montes-Atenas et al, 2010). However, the medium sized bubbles are inadequate for flotation of ultrafine particles (less than 10 μm) (Yoon and Luttrell, 1989). For these ultrafine particles fluid streamlines formed around bubbles moving upwards act as an implicit shield for particles travelling towards the bubble (Montes-Atenas et al, 2010).
This shield decreases the collision efficiency and is considered to be the main reason why the classic froth flotation process is ineffective at recovering ultrafine particles (Nguyen and Schulze, 2004; Zhou et al 1997).

There have been many studies concentrating on the flotation of fine mineral particles (e.g. Ahmed and Jameson, 1985; Anfruns and Kitchener, 1977; Dai et al., 1998; Flint and Howarth, 1971; Miettinen, 2007; Miettinen et al. 2010; Nguyen et al., 2006; Ramirez and Davis, 2001; Reay and Ratcliff, 1975; Tao, 2004; Waters et al., 2008; Yoon and Luttrell, 1989). The recovery of particles in the diameter range of 1–10 μm is improved with decreasing bubble sizes due to increased collision efficiency between particles and bubbles (Sarrot et al., 2007). Electro-flotation (denoted hereafter as EF) ensures the generation of large quantities of extremely fine and uniform gas bubbles with the average diameter around 20 μm (Bande et al, 2008). Therefore, its applications to the recovery of fine minerals and oil from oil/water emulsions have become a topic of recent research (e.g. Sarkar et al, 2010; Hosny, 1991; Osasa et al, 1992). Muller (1992) stated that for the 21st century EF would be the key electrochemically based technology.

EF can be applied for floating contaminants to the surface of a water body by small bubbles of hydrogen and oxygen generated from water electrolysis (Raju and Khangaonkar, 1984a). The use of EF in the process of mineral recovery was first proposed by Elmore in 1904 (Elmore, 1905) and was first implemented to the treatment of domestic wastewater in 1911 in the US (Siegerman, 1971). EF gained the attention of many researchers for the recovery of fine minerals since 1946 when it was first introduced to mineral beneficiation in the ex-USSR (Matis and Backhurst, 1984).
EF has the potential to eliminate the disadvantages of classical froth flotation processes. The pollutants removed from water and wastewater sources by EF have been comprehensively reported, however only a few authors (e.g. Shin, 2003) have focused on the variables that are crucial to the performance improvement. Furthermore, an in-depth review of the fundamental principles of EF, its limitations, areas that need additional improvement, future prospects, etc. are yet to be clearly addressed in the open literature. These issues are addressed in this review.

2.1 Theory of electro-flotation

2.1.1 Electrochemical reactions and electrolytic gas evolution

When an electrolyte solution is brought between two electrodes, and a direct current (dc) is passing through from the positive pole (anode) to the negative pole (cathode), an electric field is established. As a result of electrolysis reactions, hydrogen and oxygen are liberated at cathode and anode, respectively, in the form of gas bubbles. The redox reactions at the electrodes can be expressed as (Sarkar, 2012):

At the anode,

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e} \]  \hspace{1cm} (2.1)

At the cathode,

\[ 4\text{H}^+ + 4\text{e} \rightarrow 2\text{H}_2 \]  \hspace{1cm} (2.2)

The electrolysis reaction is expressed as
\[2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2\] (2.3)

Eq. (2.3) shows that the quantity of hydrogen gas generated is twice that of oxygen gas. In an electrolyte solution containing chloride (Cl\(^-\)), chlorine gas will be generated at the anode (Chen and Chen, 2010),

\[2\text{Cl}^- - 2e \rightarrow \text{Cl}_2\] (2.4)

\[\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl}\] (2.5)

\[\text{HOCl} \rightarrow \text{H}^+ + \text{OCl}^-\] (2.6)

Free chlorines (in the form of HOCl/OCl\(^-\)) are disinfectant, which is the principle of electrochemical treatment of water (Hernlem and Tsai, 2000). Furthermore some researches (e.g. Tsai et al., 2002) have shown that EF might be an attractive technology for the industries where separation and disinfection are required simultaneously.

Vogt (1983) described the physical procedure of gas evolution and divided the process into three stages: nucleation, growth and detachment. Bubbles nucleate at electrode surfaces from solutions extremely saturated (supersaturated) with electrolytic gas and grow by diffusion of dissolved gas at the bubble surface or by coalescence at electrodes with other bubbles (Sides and Tobais 1985). The bubbles detach from the electrode when buoyancy or liquid shearing forces dragging the bubbles away by overcoming their binding forces with the electrode (Khosla et al., 1991). Vogt (1983) shows that gases evolved in the electrochemical process are transferred from the electrode into the solution to a large extent by convective diffusion.
2.1.2 Effect of electrolytic gases on the surface of mineral particles

A clear understanding of the effect of electrolytic gases on the surface of mineral particles is very important for EF. The gases released from electrodes are in an active atomic state (Matis and Peleka, 2010; Raju and Khangaonkar, 1984a). Although these forms remain in the EF unit only for an extremely short period of time, gas bubbles are able to interact with mineral surfaces. Matis and Peleka (2010) stated that the free atomic oxygen generated in the diffusion layer of the anode is carried by convection into the waste water and instantly combines with the present organic and inorganic constituents, resulting in oxidation of those elements. Furthermore, Matis and Zouboulis (1995) suggested that there is also a transformation brought about by the excited hydrogen, resulting in reduction of contained constituents.

Mamakov et al. (1970) studied flotation of cassiterite (SnO₂) solids by activating the solid surface with hydrogen bubbles. The separation of cassiterite suspended in water was exceeded by 20% with compared to that of conventional air flotation. The electrodes were separated by a diaphragm to separate oxygen and hydrogen gases. Aliphatic acids were used as collectors. Hydrogen reacts with the surface of cassiterite particles according to the following Eqs. (Raju and Khangaonkar, 1984a):

\[
\text{SnO}_2 + \text{H} \rightarrow \text{SnO}_2\text{H} 
\]

\[
\text{SnO}_2\text{H} + \text{HA} \rightarrow \text{SnOA} + \text{H}_2\text{O} \quad (2.8)
\]

It was reported that the removal of diaphragm reduced the efficiency of separation of cassiterite, which might be attributed to the inactivation of cassiterite surface by oxygen.
Romanov et al. (1973) studied the EF recovery of manganese minerals (e.g. pyrolusite, psilomelane) and reported 92% to 95% recovery of manganese with hydrogen bubbles, which is 10 times greater than that of column flotation. Lazarenko (1969) reported that hydrogen is much more effective in the EF of diamond-containing ores.

It was reported by Glembotsky et al. (1975) that 98% recovery of pyrite without using any collectors since electrolytic oxygen made the surface of pyrite particles hydrophobic. Raju and Khangaonkar (1982, 1984b) have observed that oxygen gas bubbles improved the recovery of Chalcopyrite fines. Raju and Khangaonkar (1984a) concluded that EF can be effectively utilized in the separation of minerals, particularly sulphides (e.g. Mallikarjunan and Venkatachalam, 1984). Oxygen reacts with the surface of sulphide minerals, as described in the following Eq. (Raju and Khangaonkar, 1984a):

\[ \text{CuFeS}_2 + \text{O}_2 \rightarrow \text{CuS} + \text{Fe}^{2+} + \text{S} + 2e \]  

Khosla et al. (1995) have reported that the use of oxygen bubbles at any given gas evolution rate resulted in a higher flotation recovery of alumina.

Conversely, Glembotsky et al. (1975) reported that oxygen-salt minerals (such as barite, calcite, and chromite) are relatively insensitive to the type of gases (hydrogen or oxygen) and their recovery depends essentially on bubble diameters and pH of the pulp. Sometimes electrolytic gases might also act against recovery depending on the nature of minerals (Venkatachalam, 1992).
2.1.3 Effect of surface charge of particles and bubbles

The rate of flotation of particles strongly depends on the electric charge on both bubbles and suspended particles. Mineral particles are charged in aqueous solution due to possible reasons such as the ionization of surface groups, specific adsorption of ions, preferential solubility of surface ions, etc. (Miettinen et al., 2010). Gas bubbles are generally negatively charged in water and inorganic electrolytes (Li and Somasundaran, 1991). The pH at which the surface charge of the particles or bubbles is zero is called the point of zero charge or pzc. For most particles suspended in water-electrolyte solutions, if the pH of the solution is below pzc, the surface charge of particles is positive and if the pH is above pzc the surface charge is negative. The same observation has been made on air bubbles (Miettinen et al., 2010). Brandon et al. (1985) reported that the point of zero charge of air bubbles falls between pH 2 and pH 3, whereas Takahashi (2005) found the pzc of air bubbles at pH 4.

In a solution, the distribution of oppositely charged counter ions is gathered around charged particles to balance the surface charge. The surface charge on the particle/bubble and the charge of the counter ions around the particle/bubble establish the electrical double layer, as shown in Figure 2.1 (Miettinen et al., 2010). When a charged bubble and a charged particle come adjacent to each other, their diffuse layers overlay and they start to interact (Hunter, 1981). The electrostatic forces acting between particles and bubbles due to the surface charge can be calculated from their zeta potentials (the electrical potential at the plane of shear), which are routinely measured in laboratories (Yoon, 2000).

Derjaguin and Dukhin (1961) showed that when the width of the liquid film between a bubble and a particle becomes very thin, the adsorbed ions of the same charge on the two
opposite surfaces tend to keep the particle and bubble apart. Collins and Jameson (1977) measured the charges on particles and bubbles in a flotation process and proposed a simple correlation for the effect of charge on the flotation rate constant as follows:

\[-\ln \left( \frac{k_p}{d_p^{1.5}} \right) = 3.9 + 0.116 U_E U_B \]  

(2.10)

Where \( k_p \) is the rate constant (min\(^{-1}\)), \( d_p \) is the particle diameter (\( \mu \)m) and \( U_E \) and \( U_B \) are the electro-mobility (\( \mu \)m/s/V/cm) of the particle and bubble, respectively. Their results imply that the maximum rate of flotation is achieved when the zeta potential of particles is zero.

Fukui and Yuu (1980) studied the collection of submicron particles in EF and established the flotation rate dependence on the charge of both the particles and bubbles. Fukui and Yuu (1985) observed that the maximum flotation rate was achieved when the zeta potentials of the gas bubbles and particles had opposite signs. Han et al (2006) showed that the collision efficiency between bubbles and particles is highest when bubbles and particles have opposite surface charges or when zeta potentials on both were close to 0 mV. A few studies have measured the zeta potentials of particles and bubbles (e.g. Shin, 2003). Some researchers have carried out experiments to control the zeta potential of bubbles using surfactants (Yoon and Yordan, 1986). Han et al. (2004) investigated the zeta potential of electrolytic bubbles and identified factors that can produce positively charged bubbles in solution containing calcium and magnesium cations. The study concluded that in the case of calcium, the zeta potential of bubbles was negatively charged over the entire pH range. With magnesium, on the other hand, positively charged bubbles were observed at Mg concentration above 0.01 M, especially at above pH 9. The study also concluded that the zeta potential of bubbles is a function of the concentration of cations and pH of the solution.
and it may be possible to create solution conditions under which bubbles carry positive charges.

### 2.1.4 The role of hydrodynamic and surface forces

Derjaguin and Dukhin, (1961) stated that the bubble - particle collection or capture efficiency depends on three separate processes. Firstly, the particle is subjected to hydrodynamic forces, which sweep the particle around the bubble surface. Secondly, the surface forces between the bubble and particle have to rapture the thin film in order for the particle to attach to the bubble. Thirdly, the attachment forces between the bubble and particle have to be larger than the detachment forces. Particles that satisfy these three conditions can be separated selectively from other particles which do not meet one or more of the above conditions.

#### 2.1.4.1 Hydrodynamics

The behavior of fine particles in a flotation cell involves complicated hydrodynamics. The probability ($P$) of a particle being collected by an air bubble in the pulp phase of a flotation unit can be given by (Yoon, 2000):

$$P = P_c P_a (1 - P_d)$$

(2.11)

Where, $P_c$ is the probability of bubble particle collision, $P_a$ is the probability of adhesion and $P_d$ is the probability of detachment. As EF is mainly used for separation of fine particles, $P_a$ can be negligibly small because of the low inertia (Yoon, 2000), in which case Eq. (2.11) becomes:
P = P_cP_a \quad (2.12)

P_c is determined by the hydrodynamics of the system, which is strongly affected by the particle size, bubble size and turbulence of the system. On the other hand, \( P_a \) is also affected by the hydrodynamics, which is largely a function of the surface chemistry involved (Yoon, 2000).

Dai et al. (2000) presented a comprehensive review of bubble–particle collision models. However, none of these models have been verified experimentally by an EF process. Among all models, only the Gaudin (1957) model might be applicable for EF under the Stoke’s flow condition, as shown in Eq. (2.13)

\[ P_c = \frac{3}{2} \left( \frac{d_p}{d_b} \right)^2 \quad (2.13) \]

Where, \( d_p \) and \( d_b \) are the diameters of the particle and bubble, respectively. The model applies when the bubble's Reynolds number is much below unity (Schulze, 1993). Yoon (1991) verified the Gaudin model with experimental data and concluded that the model is useful for bubbles smaller than approximately 100 \( \mu \)m in diameter.

The probability of adhesion is generally modeled in terms of a contact time and an induction time (Miettinen et al., 2010). The induction time is the lowest time that is required to thin and, subsequently, to rupture the disjoining film between the bubble and the particle (Sven-Nilsson, 1934). Particle–bubble attachment occurs when the bubble–particle contact time is lengthier than the induction time (Sutherland, 1948). Both theoretical (Jowett, 1980) and experimental studies (Trahar and Warren, 1976; Ye and Miller, 1988; Li et al., 1990; Dai et al., 1999) reveal that the induction time varies with the particle diameter. Koh and
Schwarz (2006) proposed the following empirical expression for finding the induction time (sec),

\[ t_{\text{ind}} = \frac{75}{\theta} d_p^{0.6} \]  

(2.14)

Where, \( \theta \) is the contact angle in degrees and \( d_p \) is the particle dia (m). Yoon and Luttrell (1989) derived an expression for the adhesion probability:

\[ P_a = \sin^2 \left( 2 \tan^{-1} \left[ \frac{\exp \left( -\left( \frac{45 + 0.72 \text{Re}^b_{t_{\text{ind}}}}{15 d_p (d_b/d_p + 1)} \right) \right)}{15 d_p (d_b/d_p + 1)} \right] \right) \]  

(2.15)

Where, \( t_{\text{ind}} \) is the induction time, \( \text{Re}^b \) is the bubble Reynolds number (\( = \frac{d_b U_b}{\nu} \)), \( \nu \) is the kinematic viscosity, and \( U_b \) is the bubble rise velocity, which can be determined by:

\[ U_b = \frac{0.4 \varepsilon^{4/9} d_b^{7/9}}{\nu^{1/3}} \left( \frac{\rho_b - \rho_f}{\rho_f} \right)^{2/3} \]  

(2.16)

Where \( \rho_f \) is the fluid density, \( \rho_b \) is the bubble density and \( \varepsilon \) is the average energy dissipation per unit mass.

### 2.1.4.2 Surface forces

The selectivity of a flotation process depends on the surface forces. At closer distances to the particle (1-100 nm), the bubble motion is affected by at least two types of well-recognized colloidal forces: the Van der Waals and electrostatic double layer interaction forces (Yang et al, 2003). The sum of the Van der Waals and electrostatic double layer interaction forces is well-known as the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). In many flotation systems both the particles and bubbles are negatively charged. Therefore, it is unlikely that
electrostatic forces are responsible for the rupture of wetting films. Moreover the van der Waals dispersion forces are repulsive in bubble–particle interactions (Yoon, 2000). Thus, there must be a third force, i.e. the hydrophobic interaction force that is responsible for the rupture of wetting films during flotation. Therefore, the total interaction energy of a flotation unit is the sum of the Van der Waals interaction energy, electrostatic double layer interaction energy and the hydrophobic interaction energy, which is known as the extended DLVO theory (Yoon and Mao, 1996):

$$V = V_{VDW} + V_{EDL} + V_H$$  (2.17)

Van der Waals forces are universal forces, which can be calculated by the London–Hamaker microscopic approach (Hamaker, 1937; Israelachvili, 1991) as follows:

$$V_{VDW} = -\frac{A_{132}R_1R_2}{6H(R_1+R_2)}$$  (2.18)

Where $R_1$ and $R_2$ are the radii of particle and bubble, respectively, and $H$ is the shortest distance between the bubble and particle. In this expression the Hamaker constant, $A_{132}$, is the coefficient of interaction between the two spheres (1, particle and 2, bubble) that are immersed in the medium (3, water). For the contact between a particle and bubble, the Hamaker constant is negative, which consequences in a repulsive van der Waals interaction (Fielden et al., 1996; Mishchuk et al., 2002). This value can be obtained using the combining rule (Israelachvili, 1985):

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}})$$  (2.19)
Where $A_{11}$, $A_{22}$ and $A_{33}$ refer to the Hamaker constants of the solid particle, air bubble and water, respectively, in vacuum.

Miettinen et al. (2010) reviewed three approximations to calculate the electrostatic double layer interaction energy, $V_{\text{EDL}}$. The constant surface potential approximation (CPA) corresponds to the maintenance of surface chemical equilibrium, whereas the constant surface charge approximation (CCA) might be expected when the surfaces have a fixed surface charge density (Gregory, 1989). An approximation between CPA and CCA is the linear superposition approximation (LSA) (Miettinen et al. 2010). The electrostatic double layer interaction energies for particle and bubble are given as follows (Miettinen et al. 2010):

$$V_{\text{EDL-CPA}} = \frac{2\pi R_1 R_2 n_i k_B T}{(R_1 + R_2)k^2} (\phi_1^2 + \phi_2^2) \left[ \frac{2\phi_1 \phi_2}{\phi_1^2 + \phi_2^2} \ln\left(\frac{1+\exp(-kH)}{1-\exp(-kH)}\right) \right] + \ln(1-\exp(-2kH)) \quad (2.20)$$

$$V_{\text{EDL-CCA}} = \frac{2\pi R_1 R_2 n_i k_B T}{(R_1 + R_2)k^2} (\phi_1^2 + \phi_2^2) \left[ \frac{2\phi_1 \phi_2}{\phi_1^2 + \phi_2^2} \ln\left(\frac{1+\exp(-kH)}{1-\exp(-kH)}\right) \right] + \ln(1-\exp(-2kH)) \quad (2.21)$$

$$V_{\text{EDL-LSA}} = \frac{128\pi R_1 R_2 n_i k_B T}{(R_1 + R_2)k^2} \zeta_1 \zeta_2 \exp(-kH) \quad (2.22)$$

where $R_1$ and $R_2$ are the radii of particle and bubble, respectively; $\phi_1$ and $\phi_2$ in Eq. 2.20 and 2.21 (or $\zeta_1$ and $\zeta_2$ in Eq. 22) are the reduced surface potentials of the particle and bubble respectively, which are defined as $\phi = \frac{2e\psi_0}{k_B T}$ and $\zeta = \tanh\left(\frac{2e\psi_0}{4k_B T}\right)$ (Elimelech et al., 1997); $H$ is the shortest distance between the two surfaces; $k_B$ is the Boltzmann constant, $\kappa$ is the Debye–Hückel parameter, $T$ is the temperature in Kelvin, $e$ is the charge of an electron and $n_i$ is the concentration of ions. The electrostatic double layer interaction energies are
repulsive (positive) with surface potentials of the same sign and attractive (negative) with
surface potentials of the opposite sign.

Yoon and Mao (1996) described the hydrophobic interaction energy between a particle and
a bubble in the following equation:

\[ V_H = \frac{-R_1 R_2 K_{132}}{6(R_1 + R_2) H} \]  (2.23)

\( K \) can be obtained from the following relationship \( K_{132} \) (Yoon and Mao, 1996):

\[ K_{132} = \sqrt{K_{131} K_{232}} \]  (2.24)

in which \( K_{131} \) and \( K_{232} \) are the hydrophobicity constants for particle–particle and bubble–
bubble interactions in water, respectively. Their magnitudes increase with increasing
contact angle (Yoon, 2000).

From above discussion it is clear that the performance of EF can be controlled through
controlling the bubble size, surface charge of both bubble and solids, as well as
hydrophobicity of suspended particles.

2.1.5 Reagents of flotation

The previous discussion reveals that the basic principle of flotation (attachment of particles
to air bubbles) lies on hydrophobicity of minerals. Particles may be either naturally
hydrophobic (hydrocarbons and non-polar solids), or the hydrophobicity can be induced
through introducing chemicals in the suspension. The surface chemistry of the particles
and bubbles in the system are commonly controlled using collectors, activators and frothers
in the mining industry.
Collectors are organic molecules containing both nonpolar and polar chemical groups, which are adsorbed onto the mineral surface and change hydrophilic materials into hydrophobic ones (Tasker et al 2004; Mielczarski et al 1998). The formation of the bonds between collectors and mineral particles is mainly due to chemical sorption through the polar end of the collector (Klimpel, 1999). Redox properties of the collector control the modes of chemical sorption (Tasker et al 2004).

Activators are added to the flotation cell to change the surface chemistry of specific minerals and hence to facilitate collectors to adsorb onto the mineral surfaces. Suppressants behave in a similar manner to activators; however, the objective here is to alter the surface chemistry of competing minerals to enhance their hydrophilicity and hence less likely to float, thus allowing access to the desired mineral.

Frothers are another important element in flotation, which is composed of both polar and non-polar ends. Due to the heteropolar character, the frother adsorbs at the air/water interface and lowers the water surface tension and hence produces small and stable bubbles and a stable froth layer. Stabilization is important to keep bubbles well-dispersed in the slurry. The stability of the froth layer is important to avoid froth breakage before collection. Undesired breakage may cause the return of particles to the pulp.

Most often the complexity of an ore necessitates the use of a combination of collectors, activators and suppressants to achieve specific flotation. Those chemicals are frequently used for EF of minerals. Mamakov et al (1970) used aliphatic acids as collector for EF of cassiterite. Raju and Khangaonkar (1984) used Sodium diethyldithiocarbamate as a collector based on its selectivity for copper for EF of Chalcopyrite. Ketkar et al (1991) used
copper sulphate as an activator and sodium oleate as a collector for EF of quartz fines. Kydros (1994) used potassium ethyl xanthate and cetyl trimethyl-ammonium bromide as collectors and copper sulfate, ferric sulfate and potassium permanganate as modifiers for EF of pyrite. It is important to note that although collectors have been commonly used in EF applications, the use of frothers in EF has not been found in open literature by the authors, which might indicate that the electrolyte bubbles are quite stable without a frother.

2.1.6 Energy consumption

The power requirement for the EF system is the product of the current (I) and the total water electrolysis voltage (U) (Russell, 2006).

\[
\text{Power} = IU \tag{2.25}
\]

The cost of water electrolysis is proportional to the voltage applied (Wuellenweber et al, 1978). Chen et al. (2002) presented a simple equation to calculate the total voltage applied in the cell,

\[
U = E_{eq} + \eta_a + |\eta_c| + \frac{d}{k}i \tag{2.26}
\]

Where \( U \) is the electrolysis voltage (V); \( E_{eq} \) is the equilibrium potential difference for water split (V); \( \eta_a \) is the anode overpotential (V); \( |\eta_c| \) is the cathode overpotential (V); \( d \) is the inter electrode distance (m); \( k \) is the solution conductivity (S/m); and \( i \) is the current density (A/m²). From two half reactions, Eq (2.2) and Eq. (2.1), \( E_{eq} \) can be calculated from Eq. (2.27) where \( E_{H_2/O/H^+} \) and \( E_{H_2O/H^+} \) are the equilibrium potentials for cathode and anode, respectively (Sarkar, 2012),
\[ E_{eq} = (E_{H_2O/H^+}) - (E_{H_2/H^+}) \quad (2.27) \]

\[ E_{H_2/H^+} \text{ and } E_{H_2O/H^+} \text{ can be easily calculated by applying Nernst Equation (Sarkar, 2012);} \]

\[ E_{H_2/H^+} = E^0_{H_2/H^+} + \frac{RT}{2F} \ln \left( \frac{[H^+]^2}{P_{H_2}} \right) \quad (2.28) \]

\[ E_{H_2O/H^+} = E^0_{H_2O/H^+} + \frac{RT}{4F} \ln \left( \frac{(P_{O_2})[H^+]^4}{[H_2O]} \right) \quad (2.29) \]

Where, \( R = 8.31451 \text{ J/K/mol}, T = 298^\circ \text{K}, F = 96485.3 \text{ C/mol}, P_{O_2} = 1, P_{H_2} = 1 \text{ and } [H_2O] = 1, E^0_{H_2/H^+} = 0, E^0_{H_2O/H^+} = 1.23 \) and \([H^+]\) depends on the water pH.

The anode overpotential \( (\eta_a) \) and cathode overpotential \( (\eta_c) \) can be estimated by applying the Butler - Volmer Equation as follows (Sarkar, 2012):

\[ i_a = (i_0)_a \exp \left( \frac{\alpha_a \eta_a F}{RT} \right) \quad (2.30) \]

\[ i_c = - (i_0)_c \exp \left( \frac{-\alpha_c \eta_c F}{RT} \right) \quad (2.31) \]

Where, \( i_a \) and \( i_c \) are the current densities at the anode and cathode, respectively, \( (i_0)_a \) and \( (i_0)_c \) are the Standard current densities at the anode and cathode respectively, \( \alpha_a \) and \( \alpha_c \) are the anodic and cathodic transfer coefficients, respectively; and \( T \) is the absolute temperature. The Standard current densities at the anode and cathode depend critically on the nature of the electrodes, not only the structure, but also physical parameters such as the surface roughness. These values are available for different electrode materials in the literature (e.g. Sawyer et al 1995). The anodic and cathodic transfer coefficients lie in the range of 0.5 to 1.5 and can be measured experimentally. From the above equations, it is
clear that overpotentials depend on many factors, including the electrochemical properties of electrodes, current density, and the solution pH. Therefore, a direct calculation of the electrolysis voltage using Eq. (2.26) is difficult, and hence experimental measurements are recommended (Chen and Chen, 2010). Chen and Chen (2010) pointed out that the electrolysis voltage required in an EF process is mainly from the ohmic potential drop of the aqueous phase, particularly when the conductivity is low and the current density is high. Therefore, it is important to reduce the inter-electrode distance for reducing the electrolysis energy consumption. Moreover, Ibrahim et al. (2001) suggested adding table salt (NaCl) when the conductivity is low to reduce the electrolysis energy consumption.

2.2 Factors affecting electro-flotation

2.2.1 Electrolyte bubbles

Flotation is a complex process. The separation efficiency is reflected by the pollutant removal efficiency, which is largely dependent on the size of bubbles formed. Bennet et al. (1958) first reported the effect of bubble size and found that smaller bubbles are more efficient in the flotation of coal. Other studies also confirmed the role of bubble size in fine particle flotation (e.g. Ahmed and Jameson, 1985; Lee, 1969; Reay and Ratcliff, 1973 and Trahar and Warren 1976a). EF generates large quantities of finely dispersed gas bubbles, whose dimension varies between 8 and 15 μm, depending on the condition of electrolysis (Glembotsky et al. 1975). Smaller bubble sizes produce better flotation kinetics (Schubert and Bischofberger, 1978) and are specially preferred in applications because of the high surface area-to-volume ratio. Moreover, small bubbles have a higher probability of providing a smaller contact angle in a three-phase (gas-solid-liquid) system than larger
bubbles (Hanisch, 1959). A smaller contact angle produces more stable aggregates. Furthermore, the detention time of small bubbles in the flotation unit is longer than that of larger bubbles as they have a lower rising velocity. This promotes the probability of collision between gas bubbles and flocs. Conversely, the shear forces of larger bubbles are high due to the high rising velocity, which may cause the flocs to break (Jedele, 1984). Glembotsky et al. (1975) reported that electrolysis generated bubbles have a narrower bubble size distribution. Bennett et al. (1958) stated that the flotation rate can be increased not only by reducing the bubble size but also by generating more bubbles. The higher bubble flux provides more opportunity for collisions. The total number of bubbles present in the flotation cell per unit time can be determined by (Sarkar et al, 2010):

\[ N_{bT} = \frac{Q_G}{\pi d_b^3 / 6} \]  \hspace{1cm} (2.32)

Where \( d_b \) is the bubble diameter, and \( Q_G \) is the volumetric flow rate of gas which can be calculated:

\[ Q_G = Q_H + Q_O \]  \hspace{1cm} (2.33)

Where, \( Q_H \) (L/sec) and \( Q_O \) (L/sec) are the generating rates of hydrogen and oxygen, respectively, at the normal state, which can be calculated according to the Faraday’s law (Chen and Chen, 2010):

\[ Q_H = \frac{IV_o}{F_{n_H}} \]  \hspace{1cm} (2.34)

\[ Q_O = \frac{IV_o}{F_{n_O}} \]  \hspace{1cm} (2.35)
Where, $V_0$ is the molar volume of gases at the normal state (22.4L/mol); F is the Faraday’s constant (96,500 C/mol of electrons); $n_H$ is the electrons transfer number of H$_2$ (2 mol electrons per mole of H$_2$); and $n_O$ is the electrons transfer number of O$_2$ (4 mol electrons per mole of O$_2$). Therefore, the total gases generating rate is (Chen and Chen, 2010)

$$Q_G = Q_H + Q_O = \frac{IV_0}{F} \left( \frac{1}{n_H} + \frac{1}{n_O} \right) = 1.74 \times 10^{-4} I$$

Where, $Q_G$ is the total gases generating rate (L/sec) at the normal state. From Eq. (35), it is clear that the number of bubbles is directly proportional to the current density. The size of the desired bubble generation can be controlled by the current density, pH and by choosing electrodes with specific properties (Raju and Khangaonkar, 1984a). Ketkar et al (1990) also reported that EF recovery depends on combined effects of bubble diameter and bubble flux, which can be controlled by proper choice of the current density and electrode surface geometry. The following sections give an overview of the effects of different components on the bubble size in an EF process.

### 2.2.2 pH

The size variation of gas bubbles depends on the pH of water as well as the electrode material, as shown in Table 2.1 (Glembotsky et al., 1975). Raju and Khangaonkar (1984a) showed that the size of hydrogen bubbles are bigger in an acidic medium compared to that in a neutral or alkaline water. They also found that in the acid medium the effect of the cathode material on the size of bubbles is extremely noticeable, whereas the effect of the cathode material on the size of hydrogen bubbles becomes less significant in an alkaline medium. In the neutral medium the size of hydrogen bubbles is practically independent of
the cathode material. Glembotsky et al. (1973) and Brandon and Kelsall (1985a) also found the similar trend and later on Chen (2004) agreed with their results. Conversely, using a buffer solution, Llerena et al. (1996) found that between pH 3 and 4, hydrogen bubbles are the smallest (about 16±2 µm). The mean hydrogen bubble diameters were 27 µm at pH 6 and 23 µm at pH 2.

Raju and Khangaonkar (1984a) showed that oxygen bubbles formed on a platinum electrode attained a minimum size 25 µm, 30 µm and 55 µm in an acid, neutral and alkaline medium, respectively. Chen (2004) also stated that the size of oxygen bubbles increases with pH. Raju and Khangaonkar (1984a) concluded that at pH close to 6.0 the size distribution curves of both oxygen and hydrogen bubbles are very close to each other. Fukui and Yuu (1985) stated that the bubble sizes obey a log-normal distribution.

2.2.3 Current density

Current density is the most important components of EF. However, there is still disagreement among scientists regarding the effect of current density on electrolytic bubble size. Some researchers stated that the bubble size distribution is a function of the current density for a given electrode (e.g. Matov and Lazavenko 1965, Glembotsky et al. 1975 and Ketkar et al. 1988). On the other hand, Janssen and Hoogland (1970) reported that there is no significant difference in the bubble size at current densities less than 100 A/m². More recent studies (e.g. Ketar et al., 1991; Khosla et al., 1991) showed that with an increase in the current density, the bubble diameter decreases. Ketkar et al. (1988) reported that the smallest hydrogen bubbles of 22 µm were produced by using polished stainless steel plate as a cathode, at high current density (370 A/m²). Ketkar et al. (1988) found that oxygen
bubbles generated at anodes also decrease in size as the current density increases. They also stated that oxygen gas bubbles were bigger compared to the hydrogen bubbles generated under similar conditions. The sizes of gas bubbles at different current density are shown in Table 2.2 (Ketkar et al., 1991).

In contrast, some studies (e.g. Janssen and Hoogland 1970, Sides 1986 and Landolt et al. 1970) stated an overall increase in bubble diameters with an increase in the current density and attributed this to bubble merging at higher current densities. The study of Burns et al. (1997) suggested that there is no clear trend of bubble diameters as a function of current density at low values (40–210 A/m²). The study also noted that when the current densities applied to the system were increased from 100 to 1000 A/m², the diameters of oxygen bubbles increased slightly.

The uncertainty in influences of current density, have made it difficult to effectively design efficient EF systems for fine particle recovery. Therefore further study is required at reducing the uncertainty by investigating the size of bubbles produced at different current densities.

2.2.4 Electrode geometry

Matov and Lazarenko (1969) have shown that at a constant current density, the bubble diameter is related to the diameter of the electrode wire. The curvature of both anode and cathode surface influences the distribution of hydrogen and oxygen bubbles along the circumference of the electrode. Ketkar et al. (1988) showed that at constant current density and pH, the bubble diameter reduced as the wire diameter was reduced, the increase in the surface curvature results in the production of small bubbles. Glembotsky et al. (1975) also
reported a decrease in bubble diameters with the decrease in the thickness of cathode wire. Ketkar et al. (1991) have experimented on the effects of the surface geometry of electrodes. Stainless steel plates and mesh as well as platinum plates and mesh were used for cathodes and anodes, respectively. They found that the mirror polished stainless steel plate cathode generated very fine hydrogen gas bubbles. On the contrary, no significant difference in diameters of oxygen bubbles was observed between platinum plate and 200 sieve platinum mesh (Ketkar et al. 1988). Sarkar et al (2010) used the following two equations (Eq. 2.36-2.37) to determine the detachment diameter, \(d_{b,d}\), of a growing bubble from an electrode surface, which is strongly dependent on the radius of curvature, \(D/2\) (Figure 2.2) of the electrodes.

\[
d_{b,d} = \sqrt{\frac{24\sigma}{g(\rho_L - \rho_g)}} \left( \frac{\sin^2 \theta}{2 + 3\cos \theta - \cos^3 \theta} \right)
\]

\[
\theta = \frac{\omega}{1 + \sin^{-1}(d_{b,d})/D}
\]

Where \(\sigma\) is the liquid surface tension, \(\rho_L\) and \(\rho_g\) are the density of the liquid and gas, respectively and \(\omega\) is the contact angle.

2.2.5 Electrode materials

Mamakov, (1975) established the following series to relate the size of gas bubble with the electrode material.
The electrode system is considered to be the heart of an EF unit. The selection of electrode materials is more important in terms of the service life, cost and the H2 and O2 evolution overpotentials. The service life of electrode strongly depends on the current density used. An empirical relationship between the service life (SL) and the current density (i) is expressed as follows (Chen et al. 2001):

\[ SL \propto \frac{1}{i^{\alpha}} \]  

(2.38)

where, \( \alpha \) ranges from 1.4 to 2.0. The real electrode lifetime in an industrial application may be shorter due to mechanical wear.

### 2.2.6 Cathode materials

Stainless steel is a good option as it is cheap and readily available. Nickel is known to have low overpotential for hydrogen evolution. Titanium is expensive but it has long service life. Therefore those three materials are recommended as cathode by most researchers (e.g. Chen and Chen, 2010). However, Ti cannot be used without surface treatment as Ti oxidizes quickly to form titanium dioxide (TiO2) that has a low electrical conductivity.
2.2.7 Anode materials

The anode material should be chosen in such a manner that it should be practically insoluble. Though iron, aluminum, and stainless steel are cheap and easily available; those materials are consumable (easily corroded) (Alexandrova, 1994; Burns, 1997). Moreover, the bubbles generated at partially dissolved electrodes generally have larger sizes due to the coarse electrodes surfaces (Chen et al, 2002; Chen et al, 2000). Graphite and lead oxide (PbO\(_2\)) are relatively insoluble anodes used in EF (Ho and Chan, 1986; Hosny, 1996). Though they are inexpensive and readily available, they have high O\(_2\) evolution overpotential and low durability (Ho and Chan 1986). In addition, PbO\(_2\) generates highly toxic Pb\(^{2+}\), leading to the secondary pollution (Chen et al, 2002). Platinum or Pt-plated meshes are also used as anodes (Poon, 1997; Ketkar et al 1991). Though they are much more stable than graphite and lead oxide, they are costly in large scale industrial applications.

The dimensionally stable anodes (DSA) invented by Beer (1972) in the late 1960s are the most important anodes in EF. DSA use conductive precious metal oxides (RuO\(_2\), IrO\(_2\), etc.) as electro catalysts and nonconductive metal oxides (TiO\(_2\), Nb\(_2\)O\(_5\), Ta\(_2\)O\(_5\), ZrO\(_2\), etc.) as dispersing or stabilizing agents, which are coated on metal substrates (Ti, Ta, Zr, W, Nb, Bi) with a thermal decomposition method (Chen and Chen, 2010). Beer (1972) discovered the TiO\(_2\)-RuO\(_2\) based (DSA) anode, which possess a high quality chlorine evolution in the chlor-alkali industry. However, Hine et al (1979), shows that the service lives of these anodes are insufficient for oxygen evolution, as RuO\(_2\) converts easily to unstable RuO\(_4\) at high anodic potential at a low concentration of chloride ions. The major advantage of the IrO\(_x\)-based coating over the TiO\(_2\)-RuO\(_2\) mixture coating is its ability to evolve oxygen in
strongly acidic solutions while maintaining good catalytic activity and dimensional stability (Balko & Nguyen, 1991). Alves (1998) has shown that IrO$_x$ has a service life about 20 times longer than that of the equivalent RuO$_2$. In most cases, Ta$_2$O$_5$, TiO$_2$, and ZrO$_2$ are used as stabilizing or dispersing agents to save cost and to get better coating property (Cardarelli et al, 1998; Comninellis and Vercesi, 1991). Occasionally, CeO$_2$ is also used (Alves, 1994). Mraz and Krvsa (1994) and Chen et al. (2000) have successfully used Ti/IrO$_x$-Ta$_2$O$_5$ as anodes. However, it needs high percentage of Ir component; hence Ti/IrO$_x$-Ta$_2$O$_5$ electrodes are expensive, which limits their applications (Chen and Chen, 2010; Chen et al, 2002; Comninellis and Vercesi, 1991). This problem has been solved by recently developed Ti/IrO$_x$–Sb$_2$O$_5$–SnO$_2$ anodes, which have high electrochemical stability and good electro-catalytic activity for oxygen evolution (Chen et al, 2002). The service life of 2.5 mol% of IrO$_x$ is estimated to be about 8 years at a current density of 500 A/m$^2$ in acidic solutions (Chen and Chen, 2010).

2.2.8 Arrangement of electrodes

Proper arrangement of electrode is another important issue in EF technology. Multiple electrodes can be arranged in monopolar or bipolar mode as shown in Figures 2.3a and 2.3b. In an electrolytic cell, the installation of gas-evolving electrodes generally includes a vertical electrode, and horizontal electrode, as shown in Figures 2.3c and 2.3d. The vertical arrangement is preferred over the horizontal arrangement due to its easy gas releasing, easy access, installation and replacement (Wendt & Kreysa, 1999).
A conventional electrodes arrangement for EF is shown in Figure 2.4 (Chen, 2004). An anode is installed at the bottom of the cell, while a cathode is fixed above the anode (Hosny, 1996; Poon, 1997; Wendt & Kreysa, 1999). Therefore, only the upper screen cathode interacts with the wastewater flow, and the bottom anode does not contact the flow directly. Such an electrode arrangement conflicts with the aim to disperse the oxygen bubbles produced at the bottom anode immediately into wastewater flow. The process not only reduces the effectiveness of gas bubbles but also increases the probability of the breakage of the flocs formed previously, thereby reducing the flotation efficiency (Chen, 2004). In addition, to prevent short circuiting between the upper flexible cathode and the bottom anode, an inter-electrode distance of 10-50 mm is usually required. However, this large space is detrimental to the ohmic inter-electrode resistance, which would induce high energy consumption. In EF, both generation and rapid dispersion of bubbles are critical to high flotation efficiency. Therefore, the configuration of anodes and cathodes have been proposed and tested by Chen et al. (2002b), as presented in Figure 2.5 (Chen, 2004). The anode and cathode are placed on the same plane to face the wastewater flow directly. Such an open configuration allows quick dispersion of bubbles generated at both anodes and cathodes into the wastewater flow and effective attachment of bubbles on flocs surfaces. Another electrode arrangement with an open configuration is shown in Figure 2.6 (Shin, 2003) which is used for the removal of fluoride ions from industrial wastewater.
2.2.9 Particle size

The first study of the effect of particle size on flotation was done by Gaudin et al. (1942). Since then many researchers have done experimental work on the effect of particle size on air flotation (e.g. Morris, 1952; Bushell, 1962; Tomlinson and Fleming, 1963, and Flint and Howarth, 1971, Reay and Ratcliff 1973, Reay and Ratcliff, 1975, Collins and Jameson 1976, Trahar and Warren, 1976b). However, only few researchers investigated the effect of particle size on EF. Ketkar et al. (1991) studied the effect of the particle size of quartz fines on EF and reported the maximum recovery at the average particle sizes less than 10 µm.

2.3 Flotation kinetics

Flotation is generally modelled as a first-order rate process. Fukui and Yuu (1980) described the deposition of Brownian particles onto hydrogen bubbles. They suggested that the flotation rate of an EF process can be quantitatively described as follows:

\[
\frac{dC}{dt} = (\eta \left(\frac{3R_g I}{8F_a A_s P}\right) C)
\]  

(2.39)

By integrating Eq. (2.39); the total collection can be estimated as follows:

\[
E = 1 - \exp (-\eta \left(\frac{3R_g I}{8F_a A_s P}\right)t)
\]  

(2.40)

Where, C is the particle concentration, \(R_g\) is gas constant, \(F_a\) is Faraday’s constant, P is the atmospheric pressure, I is the electric current, a is the radius of bubble, T is the absolute temperature, \(A_s\) is the cross sectional area of vessel and \(\eta\) is the collection efficiency of a single bubble - defined as the fraction of particles in the bubble path which are actually
picked up by the bubble. Fukui and Yuu (1980) also suggested numerical expressions for calculating $\eta$, which is a function of London Vander walls attraction energy and double layer repulsion energy. However the hydrophobic interaction energy was ignored in their model. The theoretical total collection efficiency was experimentally verified for the EF of polystyrene latices and a close agreement was noted between the theoretical expression and the experiment (Fukui and Yuu, 1980).

Murugananthan et al (2004) fitted the kinetic data into the following kinetic models. The data were obtained during removal of suspended solids from Tannery waste water by EF using aluminum anode at a current density of 31 mA/cm$^2$:

$$R = R^* (1-e^{-kt})$$  \hspace{1cm} (2.41)

$$R = R^* \left(\frac{kt}{1+kt}\right)$$  \hspace{1cm} (2.42)

$$R = R^{*2} \left(\frac{kt}{1+R^*kt}\right)$$  \hspace{1cm} (2.43)

$$R = R^* \left[1 - \left\{\frac{ln(1+kt)}{1+kt}\right\}\right]$$  \hspace{1cm} (2.44)

Where, $R$ is the recovery at time $t$, $R^*$ is the ultimate recovery and $k$ is the rate constant. The best fit to the experimental data was observed for the first order model represented in Eq. (2.41).

Sarkar et al (2010) used Eq. (2.45) to describe the kinetic equation of EF. They considered that in EF cells, the turbulence levels are relatively low, particle-bubble detachment is negligible. This assumption was supported by Yoon and Luttrell (1989) and Tao (2004) for very fine particles (less than 10 $\mu$m).
\[ \frac{dN_{p1}}{dt} = -k_1 N_{p1} N_{bT} (1-\beta) \] (2.45)

Where \( N_{p1} \) is the number concentration \((1/m^3)\) of free particles, \( N_{bT} \) is the total number of bubbles, \( \beta \) is the average loading parameter and \( k_1 \) is the particle–bubble attachment rate constant. Koh and Schwarz (2006) provided the appropriate expressions for calculating \( k_1 \) as well as an estimate for the average loading parameter, \( \beta \).

### 2.4. Applications of electro-flotation

#### 2.4.1 Mineral beneficiation

Mineral recovery is a major application of EF (Nenno et al. 1988). The EF for the beneficiation of cassiterite was used by Mamakov et al (1970), where separation of cassiterite was exceeded by 20% compared to the conventional air flotation. The extraction of manganese (from pyrolusite and psilomelane) with electrolytically generated hydrogen bubbles was 92-95%, which was 10 times greater than column flotation (Romanov et al, 1973). EF of uranium was attempted by Turovtseva (1978), which brought the purification level to 98%. Glembotsky et al (1975) adopted EF for the recovery of fine diamonds and reported complete recovery of diamond. EF of sulphide minerals in the presence of oxygen were well established (Heye and Trahar, 1977; Gardner and Woods, 1979, Kydros et al, 1994). It has also been reported that EF provided high recoveries of ferro-cyanides, oxy-quinolates and hydroxides of Cu, Ni, Co, Ti, Zn and Mo (Nebera et al, 1980). The positive effect of oxygen on the flotation of fine chalcopyrite particles has also been reported (Raju and Khangaonkar, 1982, 1984b).
2.4.2 Oil effluents

Applications of EF are especially attractive for separation of oil from oil-water emulsions due to its low density (Matis and Peleka, 2010). In Hosny (1996)’s experimental study on separation of oil from oil–water emulsion, the oil separation reached 65% under the optimum conditions; 75% at the presence of NaCl (3.5 wt. % solution); and 92% at the presence of NaCl and under optimum concentration of flocculants. Mansour and Chalbi (2006) separated dispersed oil from oil–water emulsions in an EF cell equipped with insoluble anodes (titanium coated with ruthenium oxide). The oil removal reached 70% under the optimum condition; 75% in the presence of NaCl (3.5 wt. %); and 99.5% in the presence of both NaCl and an optimum coagulant concentration. Ibrahim et al. (2001) studied the removal of finely dispersed oil from oil–water emulsions of different Egyptian crudes by either batch or continuous processes and complete oil removal was achieved. EF has also been successful for removing oil from other oily wastewater or oil–water emulsions (Vasibenko et al, 1973; Belyacva et al, 1980; Balmer and Foulds 1986; Il’in 2002; Il’in and Sedashova 1999, Marcos et al. 2005).

2.4.3 Industrial wastewater treatment

In wastewater or industrial effluent treatment, flotation is the most effective process for the separation of low-density suspended solids (Chen and Horan 1998; Huang and Liu 1999; Lafrance and Grasso 1995; Manjunath et al. 2000; Vaughan et al. 2000). EF has wide range applications in industrial wastewater treatment as presented in the following sub-section.
2.4.4 Paint spray booths

The automotive industries produce lots of waste paint sludge which might pose an environmental hazard through the discharge of toxic substances to the environment. Therefore, Xu and Shang (2009) investigated the application of EF for separation of paint solids from automotive assembly paint booths in a series of laboratory-scale batch experiments. Their study found out that the EF process reduced the suspended solids (SS) color and chemical oxygen demand (COD). They identified that the SS criterion of <100 mg/L can be achieved by adjusting either flotation time or current density. Both operations can be easily executed. They also compared the removal efficiency of SS between the chemical coagulation and the EF treatment and showed that SS removal by the EF processes was similar to the chemical treatment. The study concluded that the EF process has the great potential for replacing coagulants and other chemicals in the treatment of process water from paint spray booths.

Yono et al (2011) have designed and patented an electrode system for EF of solids and semi-solids in paint sludge water. Each electrode of the electrode configuration is made of a non-corrosive and conductive material, such as graphite. The electrodes are operated as a polarity reversal electrode mode i.e. the anode and cathode are reversed at a predetermined time. The most important characteristic of their invention is the use of low voltage DC current for generation of electromagnetic forces to bring the solids and semi-solids to float away from the electrode array towards the surface of the paint sludge water.
2.4.5 Tannery

Wastewater from leather industry normally carries chromium, fat, surface active agents, BOD, COD and a high amount of SS (Raju and Khangaonkar, 1984a). Murugananthan et al (2004) carried out experiments for the separation of SS, COD, BOD, Sulfide, Sulfate, Pathogenic Bacteria, and chromium from tannery effluents by EF and removal efficiencies were found to be 96%, 68%, 68%, 85%, 25%, 99.97% and 99% respectively. EF was also used to remove BOD, COD and SS from wastewater of other leather industries (e.g. Mamakov et al, 1973; Revcnko and Mamakov, 1976).

2.4.6 Textile

Wastewater from dyeing and finishing processes in the textile manufacturing industry constitutes a significant source of pollution, which displays intense color, high COD, fluctuating pH, and SS (Matis and Peleka, 2010). Belkacem et al (2008) studied the removal of BOD$_5$, COD, Turbidity, SS and Color from textile wastewater, and reported the removal efficiencies of 93.5%, 90.3%, 78.7%, 93.3%, and 93% respectively. EF was also successfully used for the treatment of effluents from silk production plant (Batov et al, 1966), rayon manufacturing plant (Krainzman et al, 1974) and other textile manufacturing (e.g. Shirfin et al, 1976).
2.4.7 Food Industries

EF was used in different types of food industries (Matov et al, 1966; Andreev and Khranit, 1978, Kubritskaya et al. 2000), slaughter house (Lewandowski et al 1976), fat-containing solutions (Shendrik et al. 1993), and dairy wastewater (Rabilizirov and Gol’man 1986). Purification of waste water from beet sugar industry was attempted where the efficiency was found as high as 99% (Fedotkin, 1974).

2.4.8 Miscellaneous industries

Ho and Chan (1986) studied the EF of palm oil mill effluent in a laboratory scale. About 40% of COD was anodically destroyed, along with 86% removal of suspended particles. EF was also successfully used for the treatment of effluents containing heavy metals (Golman 1971; Kolesnikov et al. 1996; Ramadorai and Hanten 1986; Srinivasan and Subbaiyan 1989; Zelentsov and Kiselev 1986), rubber latex wastes (Binsson, 1977), effluents from wood processing industry (Ofletov et al, 1980) and wastewater from mining industry (Alexandrova et al. 1994).

2.4.9 Other Applications of EF

The use of gelatin in EF was found to aid the clarification process in apple juice industry (Araya-Farias et al, 2008). EF was also used to remove protein from fish processing (Kuji et al, 1975; Maeda et al 1975). EF was applied for rapid removal of ink from news print (Kada et al 1975). Sand et al (1974) used EF for the treatment of effluents of algae pond effectively compared with other methods of treatment. EF was used for recovery of Cr⁶⁺ from cooling tower blow down water (Demonbrun et al, 1977) as well as gold and
silver from cyanide solution (Nenno et al. 1994). EF is also found in disinfection of waste water (Sergeev et al., 1977; Hernlem and Tsai 2000) and in treating groundwater (Poon 1997), urban sewage (Il’in et al. 2002), pit waters (Zolotukhin et al. 1983), colloidal particles (Fukui and Yuu 1985), restaurant wastewater (Chen et al. 2000), and many other water and wastewaters (e.g. Camilleri 1985; Il’in and Sedashova 1999; Llerena et al. 1996).

2.5 Benefits and drawbacks of Electro-flotation

Bande et al (2008) identified three principal advantages of EF. First, dispersed gas bubbles formed from electrolysis are finer and more uniform compared to air bubbles in conventional flotation system (with the average bubble diameter around 20 µm). Second, the size and density of electrolytic bubbles can be controlled by varying current density in the flotation medium, thereby enhance the probabilities of bubble-particle collision. Third, a specific separation application can be designed via the selection of appropriate electrode surface and solution conditions to obtain optimum results. Furthermore, gas bubbles may bring changes on mineral surfaces, which may be useful in improving the flotation recovery. Table 2.3 summarizes the comparison of different treatment processes for treating different types of wastewater. EF clearly shows advantages over other techniques.

The disadvantage of EF is the pH control because OH⁻/ H⁺ ions are continuously released in to the system which might affect many of the flotation parameters, especially collector-mineral interaction and bubble size. Higher the current density is, higher the changes in the pH of the pulp will be (Raju and Khangaonkar, 1984a). The nascent gases liberating from electrodes will affect the unabsorbed reagent and also the surface compound. Since collectors sensitive to oxidation-reduction changes will be destructed due to these gases,
they should be selected accordingly. Raju and Khangaonkar, (1984a) suggested to use collectors such as xanthates because the oxidation product from xanthates, dixanthogen, is also a good collector for sulfide minerals. Electrolytic gases may act against recovery of certain minerals (Venkatachalam, 1992). A study on cassiterite showed that the EF process was 10 times more expensive than the ordinary flotation (Gol'man et al, 1971). In summary, EF can be viable where the problems cannot be solved by conventional flotation methods. Moreover, advances in electrochemistry and material science in the last few decades, such as the anode technology has made EF a feasible and cost effective technology in engineering applications.

2.6 Typical Design of Electro-flotation Unit

A brief description of EF units in various configurations can be found in Chen and Chen (2010). They mainly described three configurations of EF design: single stage, two stages and combination of EF with Electro coagulation (EC).

A single stage EF subject to a horizontal flow is often adopted due to its simplicity (Poon 1997). Chen and Chen (2010) suggested an alternative design with a vertical flow which might have higher separation efficiency due to the uniform distribution of the flow. They also suggested another type of design with two chambers (a contacting chamber and a separating chamber) to significantly reduce the electrode area. However, they pointed out a deficiency of this two-chamber design. In this unit, if the fragments dropping from the scum layer during skimming cannot be floated to the top again. A two stage EF system was suggested by Il’in and Sedashova (1999) in order to improve separation efficiency.
In order to separate dispersed fine particles effectively, EF can be combined with chemical flocculation or Electro-coagulation (EC) as shown in Figure 2.7. In such a process, EC mainly plays the role of destabilizing and aggregating fine particles, while EF is responsible for floating the flocs formed in the effluent of the EC.

2.7 Electro kinetic sedimentation and Electrophoresis

Electrokinetic remediation is a method where ions, water or charged solid particles are moved towards the electrodes under the influence of a low-voltage direct-current electric field. The main objective of electrokinetic remediation is the migration of subsurface contaminants in an imposed electric field via three phenomena as follows (Virkutyte et al 2002):

1. Electro-osmosis is the movement of pore water of soil from the anode to the cathode under the influence of an electric field.
2. Electro-migration is the movement of ions to the electrode of opposite charge under the influence of an electric field.
3. Electrophoresis is the movement of charged particles to the electrode of opposite charge under the influence of an electric field.

There are many engineering applications based on those three components of electrokinetics. However, the description of electrokinetics of this thesis is limited to electrophoresis because of the scope of the thesis.
2.7.1 Theory of electrokinetic sedimentation

The principle of electrokinetic (EK) sedimentation of clay suspension is described by Shang (1997). Clay particles carry negative charges due to the crystal structure and isomorphous substitution when they are in contact with water (Mohamedelhassan and Shang, 2001) and therefore expel when they suspended in water. Consequently, the suspension remains stable without significant settlement for a long time. When the suspension is exposed to an external dc electric field, the negatively charged particles move towards the positively charged anodes which is known as Electrophoresis (EP). Electrophoresis has been applied to accelerate sedimentation of the Welland River sediment (Buckland et al., 2000) and cohesive soils (Kim et al, 2008). Mohamedelhassan and Shang (2001) have suggested the overall particle settling velocity induced by gravity ($u_g$) and electrokinetics ($u_{EK}$):

\[ u = u_g + u_{EK} \] (2.46)

Where, for laminar flow conditions, the classic stock’s laws can be used to represent the settling velocity, $u_g$ of a single, discrete, non-flocculating particle by gravity (Metcalf and Eddy Inc, 1991):

\[ u_g = \frac{g(\rho_s - \rho_w)d^2}{18\mu} \] (2.47)

On the other hand, the velocity of individual particles induced by electrophoresis can be expressed as (Shang, 1997; Russel, 1989, Hunter, 1981):

\[ u_{EK} = \frac{\varepsilon \mu_f}{\mu} E \] (2.48)
Where $u_e$ (m/s) is the particles velocity induced by electrokinetics, $\varepsilon_w$ (F/m) is the permittivity of water, $\zeta$ (V) is the zeta potential, $\mu$ (N-s/m$^2$) is the viscosity of water, and $E$ (V/m) is the electric field intensity.

The settling velocity decreases with an increase in initial solid concentration (McRoberts and Nixon 1976). In high concentration of solids, a transition stage (hindered settling stage) between constant velocity and consolidation is observed where Stokes law cannot be applied. Therefore, Richardson and Zaki (1954) proposed an equation for high solid concentration where porosity of slurry is well below unity:

$$U = u \cdot n'$$  \hspace{1cm} (2.49)

Where $U$ is the suspensions settling velocity, $n$ represents the porosity, and $r$ is the sedimentation coefficient. However, the theory of Richardson and Zaki (1954) can be applied for the suspension of particles size more than 100 $\mu$m. Therefore a factor ($\beta$) is applied by McRoberts and Nixon (1976) as suggested by Kynch (1952) due to the effect of flow regime and the existence of high percentage of fine particles in the slurry (Buckland, 2000):

$$U = \beta \cdot u \cdot n'$$  \hspace{1cm} (2.50)

Based on Eq. (2.50), Shang (1997) has developed the equations for settling velocity at hindered settling stage induced by DC electric field by placing a cathode at the top and anode at the bottom of the settling column:

$$U_{E_k} = \beta_{E_k} \cdot \left( \frac{\varepsilon_w \zeta}{\mu \sigma j} \right) \cdot n'$$  \hspace{1cm} (2.51)
Where \( \sigma \) is the electric conductivity of water solution in S/m; and \( j \) is the current density in A/m\(^2\). Eq. (2.51) has been successfully used by many researchers (e.g. Buckland, 1999; Islam 2014).

### 2.7.2 Factors Affecting Electrokinetic sedimentation

#### 2.7.2.1 Effect of applied voltage

One of the important parameters involving to the sedimentation velocity of particles, induced by electrokinetics is the electric field intensity \( E \) (V/m) (Buckland, 1999). Buckland et al (2000), found electrokinetic sedimentation more effective at a higher electric field intensity for the range of applied voltage tested (40-150 V/m). This research also revealed that the free settling velocity and final solid concentration increased and the coefficient of sedimentation and overall sedimentation time decreased with an increase in the electric field intensity. Chung (2006) also found that the higher applied electric field strength generates faster free settling velocity. Kim et al (2008) and Alam et al (2014) also found the similar trend.

#### 2.7.2.2 Effect of zeta potential

Eq. (2.48) and Eq. (2.51) suggest that higher zeta potential has positive effect on EK sedimentation. The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If particles in suspension have a large negative or positive zeta potential then they are considered to be stable, i.e. they will repel each other and there is no affinity to flocculate (Buckland, 1999). Particles with zeta potentials higher than +30mV or lower than -30mV are normally considered stable (Shieh et al 2010).
The most important factor that changes the zeta potential of colloidal particles is pH. If the suspension has high pH, colloidal particles have an affinity to acquire more negative charges and vice versa (West and Stewart, 1995). Therefore a zeta potential versus pH curve is very important to determine the surface charge properties. Alam et al (2015) investigated the effect of pH on the EK sedimentation. This research concluded that if pH is increased by adding NaOH in the tailings slurry, the zeta potential of fine tailings become more negative, which facilitate EK sedimentation.

2.7.2.3 Effect of current intermittence

Current intermittence is a process in which the power supply is switched on and off at predetermined time intervals throughout an electrokinetic treatment (Buckland, 1999). Shang and Lo (1998) found that intermittent current improved the effectiveness and efficiency of electrokinetic dewatering of a phosphate clay. Conversely, Buckland et al (2000) and Islam (2014) found that the continuous electric current yield better electrokinetic sedimentation of Welland River sediment and mature oil sand tailings suspension respectively. Mohamedelhassen and Shang (1998) found that there is an optimum on-off ratio for a specific material for electrokinetic sedimentation. Buckland (1999) stated that the success of intermittent current depends on the soil structure (e.g. void ratio). However further study is required at reducing the uncertainty related to the current intermittence.
2.7.3 Applications of electrokinetic sedimentation

The electrokinetic phenomenon was first applied by Reuss, on clay-water mixture in 1807 (Acar and Alshawabkeh, 1993). The research on electrokinetic dewatering of tailings of coal mining was carried out by the US Bureau of Mining in the 1960s (Stanczyk and Feld 1964). The Commonwealth Scientific and Industrial Research Organization (CSIRO) also initiated research on electrokinetic dewatering of tailings in the 1970s (Lockhart 1986). Later on, electrokinetics has been successfully applied as a volume reduction of tailings and sediments (Buckland et al 2000, Shang, 1996a, 1996b) as well as a potential in-situ remediation method for contaminated soils (Acar and Alshawabkeh, 1993; Chung and Kang, 1999; Chung and Kamon, 2000a, 2000b; Hamed, 1990; Reddy and Saichek., 2002).

Shang and Lo (1997) investigated electrokinetic dewatering of phosphate clay. The findings of the research demonstrated that the sedimentation velocity can be controlled by the applied current density. The results also revealed that intermittent current and polarity reversal improved the effectiveness and efficiency of electrokinetic dewatering, reduced power consumption and neutralized adverse effect of electrode reactions.

Buckland et al (2000) carried out experiment on electrokinetic sedimentation of contaminated sediment of Welland River, Ontario. This research revealed that the application of a dc electric field on the Welland River sediment suspensions significantly increases the free settling velocity and final solid concentration and reduces the coefficient of sedimentation and overall sedimentation time.

Chung (2006) carried out experiment on dewatering and decontamination of artificially contaminated sediments (Kaolin) by using electrokinetic sedimentation. A series of
laboratory experiments under different operating conditions were performed with the Kaolin specimens mixed with ethylene glycol. This research revealed that the removal rate of contaminant was reduced with increasing applied voltage, and with decreasing solid concentration.

Kim et al (2008) demonstrated the influences of electrophoresis during EK treatment in dilute suspensions of different types of soil under different operating conditions. Their research revealed that the electrically induced surface settlement was faster with compared to that under the gravity alone.

Recently Alam et al (2014) carried out a research to assess the suitability of Electrokinetic (EK) sedimentation to accelerate sedimentation of mature fine oil sand tailings. A series of laboratory-scale column experiments were carried out to examine the effects of electrophoresis during settling processes. The research revealed that EK is feasible for accelerating sedimentation of suspended solids in fine oil sand tailings in terms of reducing the sedimentation time and increasing the final solid content.

2.8 Summary

This paper presents a state-of-the-art review on fundamental aspects that take place in the Electro-flotation and Electro-kinetic sedimentation and its applications in various fields. The following summary can be made based on this review:

- EF recovery depends on combined effects of bubble diameter and bubble flux, which can be controlled by proper choice of current density, pH, electrode materials, and electrode surface geometry. The performance of an EF system is also
dependent on power consumptions, which is governed by the electrode materials, electrode surface state as well as the operating conditions that include current density, medium electrical conductivity, and inner-electrode spacing.

- The anodes design should consider factors such as the service life, anode overpotentials, and cost. The dimensionally stable anodes (DSA) has demonstrated to be a good choice for anodes because of its high electrical conductivity, corrosion resistance, mechanical strength and reasonable costs, DSAs based on various noble metal oxide coatings have been explored and applied extensively in the industry over the past three decades and have become mature products.

- The EF comprises complex chemical and physical processes involving multiple surfaces (e.g. effect of electrolytic gases on the surface of the mineral particles) and interfacial phenomena (e.g. interaction between electrolytic bubble and particle). The scientific principles of these phenomena are yet to be fully understood. For example, there is still contradiction among researchers regarding the effect of current density (which is one of the most important parameters in EF) on bubble size. A clear understanding of those issues is very important in the engineering design of EF reactors for optimum performance and future progress of the technology.

- It is clear from the review those applications of EF are economically favourable in the extraction of disposed fine solids from waste waters, industrial effluents and in other fields. Full recovery is possible by EF on fine particles that are difficult to recover by conventional flotation processes.
• The performance of EK sedimentation depends on electric field intensity, current density, pH, zeta potential and current intermittence. This technology can be successfully applied for the volume reduction of tailings and sediments as well as a potential in-situ remediation method for contaminated soils.

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**TABLES**

**Table 2.1:** The range of gas bubbles at different pH and electrode materials (Glembotsky et al., 1975).

<table>
<thead>
<tr>
<th>pH</th>
<th>Hydrogen (µm) at Cathode</th>
<th>Oxygen (µm) at Anode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt</td>
<td>Fe</td>
</tr>
<tr>
<td>2</td>
<td>45-90</td>
<td>20-80</td>
</tr>
<tr>
<td>7</td>
<td>5-30</td>
<td>5-45</td>
</tr>
<tr>
<td>12</td>
<td>17-45</td>
<td>17-60</td>
</tr>
</tbody>
</table>
Table 2.2: The average gas bubble size from various electrodes at different current density (Ketkar et al., 1991).

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>Current density (A/m²)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>125</td>
<td>200</td>
<td>250</td>
<td>300</td>
<td>375</td>
</tr>
<tr>
<td>Hydrogen gas bubbles diameter (µm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainless steel plate</td>
<td>34</td>
<td>32</td>
<td>29</td>
<td>26</td>
<td>22</td>
</tr>
<tr>
<td>200 mesh</td>
<td>39</td>
<td>35</td>
<td>32</td>
<td>31</td>
<td>28</td>
</tr>
<tr>
<td>100 mesh</td>
<td>45</td>
<td>40</td>
<td>38</td>
<td>30</td>
<td>32</td>
</tr>
<tr>
<td>60 mesh</td>
<td>49</td>
<td>45</td>
<td>42</td>
<td>40</td>
<td>37</td>
</tr>
<tr>
<td>Oxygen gas bubbles diameter (µm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Platinum Plate</td>
<td>48</td>
<td>-</td>
<td>46</td>
<td>-</td>
<td>42</td>
</tr>
<tr>
<td>200 mesh</td>
<td>50</td>
<td>-</td>
<td>45</td>
<td>-</td>
<td>38</td>
</tr>
</tbody>
</table>
Table 2.3 Comparison of different flotation processes with Electro-flotation

<table>
<thead>
<tr>
<th>Treatment process/Parameter</th>
<th>Electro-flotation (EF)</th>
<th>Dissolved air flotation (DAF)</th>
<th>Impeller flotation (IF)</th>
<th>Settling/Sedimentation</th>
<th>Foam flotation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Purification of oily wastewater:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Il’in &amp; Sedashova, (1999)</td>
</tr>
<tr>
<td>Bubble diameter, μm</td>
<td>1-30</td>
<td>50-100</td>
<td>0.5-2</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific power consumption, W/m³</td>
<td>30-50</td>
<td>50-60</td>
<td>100-150</td>
<td>50-100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air consumption (m³/m³) water</td>
<td>-</td>
<td>0.02-0.06</td>
<td>1</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical conditioning</td>
<td>IC</td>
<td>OC+F</td>
<td>OC</td>
<td>IC+F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process duration, min</td>
<td>10-20</td>
<td>30-40</td>
<td>30-40</td>
<td>100-120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume of sludge, %</td>
<td>0.05-0.1</td>
<td>0.3-0.4</td>
<td>3-5</td>
<td>7-10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil removal efficiency, %</td>
<td>99-99.5</td>
<td>85-95</td>
<td>60-80</td>
<td>50-70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SS removal efficiency, %</td>
<td>99-99.5</td>
<td>90-95</td>
<td>85-90</td>
<td>90-95</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Purification of radioactive wastewater:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Il’in &amp; Kolesnikov, (2001)</td>
</tr>
<tr>
<td>Process duration, h</td>
<td>0.2-0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Purification efficiency, %</td>
<td>92-95</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture of sediment, %</td>
<td>92-95</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>98.5-99.8 92-96.5</td>
</tr>
<tr>
<td>Volume of sediment, %</td>
<td>0.1-0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17-18 3.3-3.5</td>
</tr>
</tbody>
</table>

Purification of porcelain and faience industrial sewage:
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th>II’ in et al., (2002)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process duration, h</td>
<td>0.2-0.4</td>
<td>2.0-7.0</td>
<td></td>
</tr>
<tr>
<td>Consumption of coagulant, g/l</td>
<td>0.02-0.04</td>
<td>0.20-0.40</td>
<td></td>
</tr>
<tr>
<td>Purification efficiency, %</td>
<td>95-99</td>
<td>70-80</td>
<td></td>
</tr>
<tr>
<td>Moisture of sediment, %</td>
<td>92.0-95.0</td>
<td>98.5-99.8</td>
<td></td>
</tr>
<tr>
<td>Volume of sediment, %</td>
<td>0.1-0.2</td>
<td>17.0-20.0</td>
<td></td>
</tr>
</tbody>
</table>

Note: SS = Suspended solids; IC = Inorganic coagulants; OC = Organic coagulants; F = Flocculants
Figure 2.1 The Stern–Grahame model of the electrical double layer (Miettinen et al, 2010)
Figure 2.2: Geometry for bubble on curved electrode surface (Sarkar et al., 2010)
Figure 2.3: Schematic diagrams of electrodes arrangement: (a) Monopolar; (b) Bipolar; (c) Vertical; (d) Horizontal.
Figure 2.4: Conventional electrode arrangement for electroflotation (Chen, 2004).
Figure 2.5: Novel electrode arrangement for electro-flotation (Chen, 2004).
Figure 2.6: Alternative electrode arrangement for Electro-flotation (Shin, 2003).
Figure 2.7: Combined EC–EF (Chen and Chen, 2010)
CHAPTER 3

ELECTROCHEMICAL MODEL OF ELECTRO-FLOTATION

3 Introduction

Electro-flotation (EF) is an electrochemical technology that is effective in separation of solids and liquids, such as fine slimes of low grade ores, domestic and industrial waste water, by means of hydrogen and oxygen gas bubbles generated from water electrolysis. Bande et al (2008) identified three principal advantages of EF. First, dispersed gas bubbles formed from electrolysis are finer and more uniform compared to air bubbles in conventional flotation system. Second, the size and density of electrolytic bubbles can be controlled by varying current density in the flotation medium, thereby increasing the probabilities of bubble-particle collision. Third, a specific separation application can be designed via the selection of appropriate electrode surface and solution conditions to obtain optimum results. Therefore, its applications to the recovery of fine minerals and oil from oil/water emulsions have become a topic of recent research (e.g. Sarkar et al, 2010; Xu and Shang, 2009, Bande et al, 2008). Muller (1992) stated that for the 21st century EF would be the key electrochemically based technology.

The operating cost is one of the primary concerns for the performance of an EF system. Operating cost depends on the power consumption that is strongly reliant on the electrolysis voltage and current. The electric power of an electro-flotation cell can be obtained by multiplying the cell voltage with current. For a higher current, which is more likely applied
for electro flotation, any small raise of the cell voltage can cause a severe rise in the power demand. Therefore, the prediction of electrolysis voltage under desired operating conditions is very important for industrial applications. Although EF has been practiced since 1900s (Elmore, 1905), a comprehensive electrochemical model to simulate electrolysis voltage in an electro-flotation cell has not been reported in the literature. A simple model involving terms of activation overpotential, concentration overpotential and ohmic overpotential of the solution resistance was proposed by several researchers (e.g. Scott, 1995). However, the prediction of the unknown terms needs to be addressed more specifically, such as the activation overpotential and the concentration overpotential. Moreover the bubble effect on the overall electrical resistance in an electro-flotation cell needs to be considered. In this study, a simplified analytical model has been derived for the estimation of electrolysis voltage of an electro-flotation cell based on Nernst equation, Tafel equation, Fick’s model, and Ohm’s law, considering both the activation overpotential and concentration overpotential. The effect of bubbles in an electro-flotation cell is also considered in the theoretical model, which is an enhancement to previous studies (e.g. Chen et al, 2002a).

The objectives of this study is to derive the theoretical models regarding the electrolysis voltage required in an electro-flotation process and to verify the simulation results by comparing with experimental data from both this study as well as data obtained from the literature.
3.1 Electrochemical model

When an electrolyte solution is brought between two electrodes with opposite electric charges, a direct current (dc) is passing through from the positive pole (anode) to the negative pole (cathode), and an electric field is established. As a result of electrolysis reactions, hydrogen and oxygen gases are formed and liberated at cathode and anode, respectively, in the form of gas bubbles.

The oxygen evolution reaction at the anode is (Sarkar, 2012)

\[ \text{2H}_2\text{O} - 4\text{e} \rightarrow \text{O}_2 + 4\text{H}^+ \quad \text{E}^\circ_A = +1.23 \text{ V} \]  \hspace{1cm} (3.1)

The hydrogen evolution reaction at the cathode is (Sarkar, 2012)

\[ 4\text{H}^+ + 4\text{e} \rightarrow 2\text{H}_2 \quad \text{E}^\circ_C = 0 \text{ V} \]  \hspace{1cm} (3.2)

The overall electrolysis reaction is expressed as

\[ \text{2H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2 \quad \text{E}_{\text{eq}} = +1.23 \text{ V} \]  \hspace{1cm} (3.3)

The operating current in an electro-flotation cell must exceed the equilibrium potential difference, anode overpotential, cathode overpotential, and ohmic overpotential of the solution in order to maintain electrochemical reactions (Scott, 1995), as shown in Eq. (3.4).

\[ \text{E}_{\text{cell}} = \text{E}_{\text{eq}} + \eta_a, a + \eta_a, c + \eta_a, p + |\eta_c, a| + |\eta_c, c| + \eta_{\text{ohm}} \]  \hspace{1cm} (3.4)
where $E_{\text{cell}}$ is the electrolysis voltage (V); $E_{\text{eq}}$ is the equilibrium potential difference for water split (V); $\eta_{\text{a,a}}$ is the anode activation overpotential (V), $\eta_{\text{a,c}}$ is the anode concentration overpotential (V), $\eta_{\text{a,p}}$ is the anode passive overpotential (V), $\eta_{\text{c,a}}$ is the cathode activation overpotential (V) and $\eta_{\text{c,c}}$ is the cathode concentration overpotential (V) and $\eta_{\text{ohm}}$ is the ohmic overpotential (V). For a new electrode system the passive overpotential is negligible i.e. $\eta_{\text{a,p}} = 0$. The typical voltage components in an electro-flotation cell are shown Figure 3.1.

### 3.1.1 Equilibrium voltage

The equilibrium voltage of an electro-flotation cell can be expressed by the Nernst equation (Sarkar, 2012):

At anode:

$$E_A = E_A^0 + \frac{RT}{nF} \ln \left( \frac{P_{O_2}}{[H_2O]} \right)^4$$

At cathode:

$$E_C = E_C^0 + \frac{RT}{nF} \ln \left( \frac{[H^+]^2}{P_{H_2}} \right)$$

where $E_A^0$ and $E_C^0$ are the equilibrium potentials of anode and cathode, respectively, under standard conditions ($T = 298$ K, $P = 1$ atm and $[H^+] = 1$ M (i.e. at pH 0)), $R = 8.314$ J/K mol, is the ideal gas law constant, $T$ is the absolute temperature, $n$ is the amount of electrons involved in the reaction (at anode $n = 4$ and at cathode $n = 2$) and $F$ is the Faraday constant (96,485 C/mol).
The equilibrium potential difference between the anode and the cathode is

$$E_{eq} = E_A - E_C$$  \hspace{1cm} (3.7)

Thus,

$$E_{eq} = \left[ E^0_A + \frac{RT}{nF} \ln \left( \frac{(P_{O_2})[H^+]^4}{[H_2O]} \right) \right] - \left[ E^0_C + \frac{RT}{nF} \ln \left( \frac{[H^+]^2}{P_{H_2}} \right) \right]$$  \hspace{1cm} (3.8)

### 3.1.2 Activation overpotential

The activation overpotential is related to the electrode kinetics at the reaction site, which represents the overpotential incurred due to the activation energy necessary for charge transfer (Meng et al 2006). The anode activation overpotential ($\eta_a$) and cathode activation overpotential ($\eta_c$) can be estimated by applying the Tafel Equation as follows (Chen et al 2002b):

$$\eta_{a,a} = a_a + b_a \ln j$$  \hspace{1cm} (3.9)

$$\eta_{c,a} = a_c + b_c \ln j$$  \hspace{1cm} (3.10)

where, $j$ is the current density (A/m$^2$), $a_a$ and $a_c$ are the constant of Tafel equation at the anode and cathode respectively, and $b_a$ and $b_c$ are Tafel slope of Tafel equation at anode and cathode, respectively.
3.1.3 Concentration overpotential

The concentration overpotential is caused by the resistance to the transport of reactant species approaching the reaction site, and the transport of product species leaving the reaction site (Meng et al 2006). In the present study, the equations of concentration overpotential in an EF system are derived based on a previous study of Chen et al (2002b).

In an electrochemical reaction, the mass transport, \( J_m \) includes diffusion \((-D_m\frac{\partial C_m(x)}{\partial x})\), convection \( (C_m(x) v(x)) \) and electric migration \( (t_m j) \), and can be calculated based on the Nernst–Plank equation (Chen et al, 2002b):

\[
J_m (x) = -D_m\frac{\delta C_m(x)}{\delta x} + C_m(x) v(x) + t_m j
\]  

(3.11)

Where \( J_m (x) \) is the net flux of a species m, \( D_m \) is the diffusion coefficient of species m, \( m^2/s \), \( C_m(x) \) is the concentration of species m at distance x, (mol/L), \( v(x) \) is the convective velocity of water flow in the current direction at distance x, m/s, \( t_m \) is the transport number of species m and \( j \) is the current density (A/m²).

Within the diffusion layer adjacent to the electrode surface, non-reactive ions coming from electrolyte (e.g. Na⁺ or SO₄⁻) and other sources (such as water or wastewater) produce a gradient of concentration and thus cause diffusion current (Chen et al, 2002b). However, the current from those non-reactive ions are equal but opposite to the migration current at steady state (Chen et al, 2002b). Therefore the net transport and the net current from those non-reactive ions are considered to be zero (Chen et al, 2002b). Figure 3.2 illustrates the concentration variation of reactive ions H⁺ and OH⁻ near the anode and cathode. As the concentration of H⁺ near the anode is relatively high, the total current in the anode
diffusion layer is composed primarily of the migration and diffusion of $H^+$. On the other hand, as the concentration of $OH^-$ near the cathode is much higher than that of $H^+$, the current comes predominantly from the diffusion and migration of $OH^-$. Near the electrode surface, the convective flux term ($C_m(x) v(x)$) can be ignored (Scott, 1995). Moreover, at a high electrical conductivity, $t_{H^+}$ and $t_{OH^-}$ approach zero (Chen et al, 2002b). Therefore Eq. (3.11) becomes Eq. (3.12), which is widely known as the Fick’s model:

$$J_m(x) = -D_m \frac{\delta C_m(x)}{\delta x}$$  \hfill (3.12)

### 3.1.3.1 Concentration overpotential at anode

Under the assumption that the $H^+$ concentration varies linearly across the whole diffusion layer at anode,

$$\frac{\delta c}{\delta x} = \frac{[C_{H^+}|_{x=0}]-[C_{H^+}]}{\delta_a}$$  \hfill (3.13)

Where, $C_{H^+}|_{x=0}$ is the concentration of $H^+$ at the anode surface, $C_{H^+}$ is the bulk concentration of $H^+$, and $\delta_a$ is the diffusion layer thickness at the anode. At the anode Eq. (3.12) becomes

$$J_{H^+} = \frac{D_{H^+}[C_{H^+}|_{x=0}]-[C_{H^+}]}{\delta_a}$$  \hfill (3.14)

Where $J_{H^+}$ is the flux of $[H^+]$ (mol/m² s¹), $D_{H^+}$ is the diffusion coefficient of the $[H^+]$ (m²/s). Hence the current density, $j$, as a function of mass transport flux at the anode can be expressed as (Chen et al, 2002b):

$$j = z \cdot F \cdot J_{H^+} = \frac{Z \cdot F \cdot D_{H^+}[C_{H^+}|_{x=0}]-[C_{H^+}]}{\delta_a}$$  \hfill (3.15)

Where, $z$ is the number of electron in the half reaction.
Usually, at anode, \([\text{C}_\text{H}^+|_{x=0}] \gg [\text{C}_\text{H}^+]\); hence Eq. (3.15) becomes:

\[
j = \frac{Z.F.D_{H^+}[\text{C}_\text{H}^+|_{x=0}]}{\delta_a}
\]

(3.16)

Thus, \([\text{C}_\text{H}^+|_{x=0}] = \frac{j\delta_a}{Z.F.D_{H^+}}\)

(3.17)

The concentration overpotential at anode is:

\[
\eta_{c,a} = \left(\frac{2.3RT}{nF}\right) \log \left(\frac{[\text{C}_\text{H}^+|_{x=0}]}{[\text{C}_\text{H}^+]}\right)
\]

(3.18)

Replacing \([\text{C}_\text{H}^+|_{x=0}]\) in Eq. (3.18):

\[
\eta_{c,a} = \left(\frac{2.3RT}{nF}\right) \log \left(\frac{j\delta_a}{[\text{C}_\text{H}^+].Z.F.D_{H^+}}\right)
\]

(3.19)

Eq. (3.19) can be used to calculate the concentration overpotential of an electro-flotation cell at the anode.

3.1.3.2 Concentration Overpotential at cathode

Similarly, assuming the \(\text{OH}^-\) concentration varies linearly across the diffusion layer at the cathode,

\[
\frac{\delta c}{\delta x} = \frac{[c_{\text{OH}^-}|_{x=0}]-[c_{\text{OH}^-}]}{\delta c}
\]

(3.20)

Where, \(c_{\text{OH}^-}|_{x=0}\) is the concentration of \(\text{OH}^-\) at the cathode surface, \(c_{\text{OH}^-}\) is the bulk concentration of \(\text{OH}^-\), and \(\delta c\) is the diffusion layer thickness at cathode. At the cathode Eq. (3.12) becomes
\[ J_{OH^-} = \frac{D_{OH^-} \left( \left[ OH^- \right]_{x=0} \right) \left( \left[ OH^- \right] \right)}{\delta_c} \quad (3.21) \]

Where \( J_{OH^-} \) is the flux of \([OH^-]\) (mol/m² s), \( D_{OH^-} \) is the diffusion coefficient of the \([OH^-]\) (m²/s). Hence the current density, \( j \) as a function of mass transport flux at cathode can be expressed as (Chen et al., 2002b):

\[ j = z \cdot F \cdot J_{OH^-} = \frac{Z \cdot F \cdot D_{OH^-} \left( \left[ OH^- \right]_{x=0} \right) \left( \left[ OH^- \right] \right)}{\delta_c} \quad (3.22) \]

At the cathode, usually \( [OH^-]_{x=0} >> [OH^-] \) therefore the Eq. (3.22) becomes:

\[ j = \frac{Z \cdot F \cdot D_{OH^-} \left( \left[ OH^- \right]_{x=0} \right)}{\delta_c} \quad (3.23) \]

Thus \( [OH^-]_{x=0} = \frac{j \delta_c}{Z \cdot F \cdot D_{OH^-}} \quad (3.24) \]

The concentration overpotential at the cathode (Chen et al., 2002b):

\[ \eta_{c,c} = \left( \frac{RT}{nF} \right) \log \frac{[H^+]_{x=0}}{\left[ H^+ \right]_{x=0}} \quad (3.25) \]

Where, \( \left[ H^+ \right]_{x=0} \) is the concentration of H⁺ at the cathode surface. \( \left[ H^+ \right]_{x=0} \) can be replaced in terms of the ionic product for water, \( K_w \), as follows (Chen et al., 2002b):

\[ \left[ H^+ \right]_{x=0} = \frac{K_w}{[OH^-]_{x=0}} \quad (3.26) \]

Hence, \( \left[ H^+ \right]_{x=0} = \frac{K_w Z \cdot F \cdot D_{OH^-}}{j \delta_c} \) (by replacing \( [OH^-]_{x=0} \) in Eq. (3.26) from Eq. (3.24))

Therefore Eq. (3.25) becomes:
\[ \eta_{c,c} = \left( \frac{2.3RT}{nF} \right) \log \frac{[c_{H^+}]j\delta_c}{K_wZ_FD_{OH^-}} \]  

(3.27)

Eq. (3.27) can be used to calculate the concentration overpotential of an electro-flotation cell at the cathode.

### 3.1.4 Ohmic overpotential

According to the Ohm’s law, the ohmic overpotential of an electro-flotation cell can be expressed as:

\[ \eta_{ohm} = R \cdot i \]  

(3.28)

Where, \( i \) and \( R \) represent the local current and local electrochemical cell resistance, respectively. In the absence of bubbles, the cell resistance \( R \) can be calculated by Eq. (3.29),

\[ R = \rho \frac{d}{A} \]  

(3.29)

Therefore, Eq. (3.28) becomes

\[ \eta_{ohm} = \rho \frac{d}{A} i \]  

(3.30)

Where, \( \rho \) is the Electrical Resistivity (\( \Omega \cdot m \)), which is a reciprocal to the electrical conductivity (\( \sigma \)), \( d \) is the distance between the anode and cathode (m), \( A \) is the surface area of electrode (m\(^2\)). In an electro-flotation cell, bubbles are produced, which affect the overall electrical resistance. Because bubbles have negligible conductivity compared to the electrolyte, they reduce the conductivity of the system and cause the increase of the ohmic losses (Cooksey et al., 2008). Several approaches have been suggested to calculate the
modified electrochemical cell resistance $R_x$ due to the effect of bubbles (Cooksey et al, 2008), which can be used in an electro-flotation cell as follows:

$$R_x = \frac{1}{\sigma A} \left[ \frac{h}{1 - \theta} + (d - h) \right]$$

(3.31)

$$R_x = \frac{1}{A} \left[ \frac{h}{\sigma_x} + \frac{(d-h)}{\sigma} \right]$$

(3.32)

Where, $\theta$ is the area fraction of electrode covered by bubbles (for the simplicity, in the present model it is assumed that for both anode and cathode, the area fraction of electrode covered by bubbles are equal to $\theta$, $h (= h_1 + h_2)$ is the thickness of bubble layer as shown in Figure 3.3, $\sigma_x$ is the electrical conductivity of the gas–liquid dispersion and $\sigma$ is the electrical conductivity of bubble-free liquid. Several theoretical equations are available to describe the relationship between $\sigma_x$ and $\sigma$, of which the most familiar are the Maxwell equation (Maxwell, 1892):

$$\frac{\sigma_x}{\sigma} = \frac{1 - \varepsilon}{1 + \frac{\varepsilon}{2}}$$

(3.33)

and the Bruggeman equation (Bruggeman, 1934)

$$\frac{\sigma_x}{\sigma} = (1 - \varepsilon)^{3/2}$$

(3.34)

Where, $\varepsilon$ is the volume fraction of bubbles which has a relationship with $\theta$ (Vogt, 2003):

$$\varepsilon = \frac{2}{3} \theta$$

(3.35)

Therefore, by replacing the cell resistance, $R$ by the modified electrochemical cell resistance $R_x$; Eq. (3.28) becomes

$$\eta_{ohm} = R_x i$$

(3.36)

Now, combining Eqs. (3.8, 3.9, 3.10, 3.19, 3.27 and 3.36); Eq. (3.4) can be rewritten as
\[
E_{\text{cell}} = E_0^A + \frac{RT}{4F} \ln \left( \frac{(P_{O_2})[H^+]^4}{[H_2O]} \right) - E_0^C - \frac{RT}{2F} \ln \left( \frac{[H^+]^2}{P_{H_2}} \right) + (a_a + b_a \ln j) + \\
\left( \frac{2.3RT}{nF} \right) \log \frac{j_{\delta_a}}{[C_{H_4}]Z.F.D_{H_4}^+} + (a_c + b_c \ln j) + \left( \frac{2.3RT}{nF} \right) \log \frac{[C_H^+]}{K_{w_4}Z.F.D_{OH}^-} + (R_x) i
\]  

Eq. (3.37) is the proposed model to predict the cell voltage for the electro-flotation. Using \( j \) (and \( i \)) as the independent variable, the numerical values of corresponding ohmic overpotential, activation overpotentials, concentration overpotentials, as well as the cell equilibrium potential can be computed by substituting the measured values into the right-hand side of the equations. The measured values of \( R_x \) can be applied in either Eq. (3.31) or Eq. (3.32).

### 3.2 Experimental

#### 3.2.1 Electrode materials

Iridium dioxide coated titanium (Ti) plates (ELTECH System Co), was used as the anode for the study. Figure 3.4 shows the result of X-ray Photoelectron Spectroscopy (XPS) analysis of the Ti/IrO\(_x\)-anode. Tantalum and Iridium were found on surfaces as Ta (V) and Ir (IV), which reveals that IrO\(_2\) was used as conductive precious metal oxides, as electrocatalysts (i.e. participates in electrochemical reactions) and Ta\(_2\)O\(_5\) was used as a nonconductive metal oxide as dispersing or stabilizing agent as a coating of Ti. Stainless steel SS 316 was selected as the cathode for the study. The electrochemical properties of both electrodes are available in open literature ((Mraz and Krysa, 1994; Kelly et al, 2008).
3.2.2 Solution preparation

In this study, the solution used in the test was prepared by dissolving Na$_2$SO$_4$ in tap water, which has the conductivity of 210-230 $\mu$s/cm. Na$_2$SO$_4$ is added to the solution as a supporting electrolyte for the sole purpose of adjusting the solution conductivity to 2100 $\mu$s/cm. Since the dispersed particles usually do not take part in the electrochemical reactions (Chen et al., 2002b), the electrochemical behavior of the aqueous solution of the present study (synthesized with Na$_2$SO$_4$) is expected to be identical to the real water/wastewater experiment.

3.2.3 Electrodes system

As mentioned earlier, the Ti/IrO$_2$-Ta$_2$O$_5$ anode and SS316-cathode combination were selected to fabricate electrode modules in the present study. Figure 3.5 shows the test setup for the overpotential measurement. The potential measurements were made at four locations as shown in Figure 3.5 (b). The anode-cathode spacing varied from 20 mm to 95 mm. As shown in Fig 3.5, the voltage drop near anode and cathode were measured using two coated this copper rods installed as close as possible to the electrodes at point 2 and point 3, respectively. The gap between point 1 and 2 is the same as for point 3 and 4, which is 0.25mm. Therefore, the anode and cathode overpotentials can be calculated from $E_{12}$ (voltage between points 1 and 2) and $E_{34}$ (voltage between points 3 and 4), respectively, using Eq. (3.38) and Eq. (3.39). Similarly, the experimental ohmic overpotential can be calculated from $E_{23}$ (voltage between points 2 and 3) from Eq. (3.40). Therefore, $E_{14}$ (voltage between points 1 and 4) represents the total experimental cell potential which is also the summation of $E_{12}$, $E_{23}$ and $E_{34}$. As the copper rod was installed outside of the
diffusion layer (the diffusion layer usually lies between 0.1 mm to 0.001 mm, Janssen and Hoagland, 1970) there will be an ohmic loss ($E_{\text{at } 0.25 \text{ mm}}$) between the electrode and the copper rod, which is calculated by extrapolating the straight line going through points 2 and 3 as shown in Figure 3.6. The voltage of each cell between the electrodes was measured by a voltage meter (Fluke 27 Multimeter). The total current for the circuit was maintained by a DC power supply (HP 6545A).

The experimental anode overpotential of Ti/IrO$_2$-Ta$_2$O$_5$ was measured by the following relationship:

$$\eta_{\text{anode}} = E_{12} - E_{A} - E_{\text{at } 0.25 \text{ mm}}$$

(3.38)

Where, $\eta_{\text{anode}}$ is the anode overpotential. The Equilibrium potential at anode, $E_{A}$ is calculated from Eq. (3.5). Similarly, the overpotential of SS 316 cathode was measured by the following relationship:

$$\eta_{\text{cathode}} = E_{34} - |E_{C}| - E_{\text{at } 0.25 \text{ mm}}$$

(3.39)

Where $\eta_{\text{cathode}}$ is the cathode overpotential, the Equilibrium potential at cathode, $E_{C}$ is calculated from Eq. (3.6). The experimental ohmic overpotential was expressed in the following relationship:

$$\eta_{\text{ohm}} = E_{23} + 2E_{\text{at } 0.25 \text{ mm}}$$

(3.40)
3.3 Results and discussions

3.3.1 Effect of bubbles

According to Eq. (3.29), by reducing the distance between electrodes, a lower electrical resistance can be achieved. However, placing the electrodes too close to each other would increase the void fraction due to the high density of bubbles and therefore, lead to higher electrical resistance (Nagai et al., 2003, LeRoy et al., 1979). In the present study, to assess the effect of inter electrode spacing on the electro-flotation cell voltage, a series of tests were performed. Figure 3.7 shows the effect of inter-electrode spacing (for 20 mm and 95 mm) on the ohmic overpotentials between experimental data and Eq. (3.30). It is important to mention that in Eq. (3.30), the ohmic overpotential was calculated without considering the bubble effect. It was found that for the electrode spacing of 95 mm, the experimental ohmic overpotentials were within 15% of that predicted by Eq. (3.30). On the other hand, for the electrode spacing of 20 mm, the experimental ohmic overpotentials were more than 40% of that predicted by Eq. (3.30). This indicates the effect of the void fraction at lower inter-electrode spacing. Another important observation is that the gap between the experimental data and results predicted by Eq. (3.30) increases with increasing current density (A/m²). This is reasonable because at a higher current density, the bubble density increases, which increases the electrical resistance and hence ohmic overpotential.

The effect of bubbles on the electrical resistance of an electro-flotation unit can be established by studies of the relationship between resistance and inter-electrode spacing. If bubbles have no effect, then the resistivity of the electrolyte should be constant and independent of the inter-electrode spacing (Cooksey et al, 2008). In the present study, it is found that the resistivity increased with decreasing inter electrode spacing, and became
asymptotic at a spacing approximately 10 to 15 mm (Figure 3.8). Hence it can be assumed that the bubble layer thickness was approximately between 10 and 15 mm, which are comparable to the thickness reported in the literature (e.g. 10 mm in Houston et al., 1988; 21 mm in Haupin, 1971). Therefore, electrode covered by bubbles can be estimated by the Eq. (3.31). The electrode covered by bubbles was calculated to be 42% to 52% with a standard deviation of 3.6 % for different electrode spacing (20 mm to 95 mm). And the corresponding bubble fraction between the electrodes was estimated to be 25% to 35% by Eq. (3.35), which significantly increases the cell resistance and hence overall cell potential.

As mentioned earlier that the bubble coverage and the volume fraction of bubbles change the conductivity of the electrolyte/air bubble mixture within the bubble layer thickness. Therefore it is very important to know the reduction of the conductivity, $\sigma_x$ due to the gas component. Most expressions found in the literature related to $\sigma_x$ are a function of the volume fraction of bubbles ($\varepsilon$) as shown in Eqs. (3.33-3.34). Eq. (3.33), known as the Maxwell equation, is used for equal-sized bubbles, on the other hand Eq. (3.34), known as the Bruggeman equation, is used for bubbles of unequal size (Cooksey et al, 2008). The relationship between the resistance (using Maxwell Eq., Bruggeman Eq., Eq. (3.29) and experiment) and the inter electrode spacing for conductivity of 2100 $\mu$s/cm is shown Figure 3.9. It is seen that within the experimental conditions in this study, the resistances are linearly related to the inter electrode spacing in all cases. It was found that the experimental resistance was close to the resistance predicted by the Bruggeman equation (within 5%), which reveals that most of the bubbles are unequal sizes. Moreover the significant variation between the experimental resistance and the resistance calculated from Eq. (3.29) (without
considering the bubble effect) reveals that in the electro-flotation cell model bubble effect cannot be ignored.

### 3.3.2 Simulation

The Tafel slope for Ti/IrO$_2$-Ta$_2$O$_5$ as anode is reported as 76 mV (Mraz and Krysa, 1994). On the other hand, Tafel slope for SS-316 as cathode is reported as 149 mV (Kelly et al, 2008). The Bubble coverage, $\theta$, was taken as 45% from experiments as described in the previous section and the corresponding void fraction ($\varepsilon$) is taken as 30%. The thickness of bubble layer ($h=h_1+h_2$) is taken as 1.2 cm (Figure 3.8). The Diffusivity coefficient for H$^+$ and OH$^-$ are available in the literature as $9.3 \times 10^{-5}$ (cm$^2$/sec) and $5.25 \times 10^{-5}$ (cm$^2$/sec) respectively (e.g. Baniasadi et al. 2013). The ion product of water, $K_w$, is $10^{-14}$ (Sawyer et al, 2003). The Diffusion layer thickness is a function of current density, which is approximated as (Janssen and Hoogland, 1970):

$$\delta_c = -0.012j + 11.2 \quad \text{and} \quad \delta_a = -0.001j + 4.105$$

The developed model (Eq. 37) for the electro-flotation cell can be validated by comparison with experimental data. A set of experiments, which were not used to measure the bubble coverage and bubble fraction, is conducted under various conditions, including different conductivities (5730 µs/cm to 18,000 µs/cm), inter-electrode spacing (20-300 mm), and current densities (20-180 A/m$^2$). Figure 3.10 shows a comparison between the predictions by Eq. (3.37) (the Bruggeman Eq) and experimental results. It is seen that the predictions are in good agreement with the experimental results.

The Current density and Cell voltage relationship is widely used to validate different types of electro-chemical cell models, such as electro-coagulation (Chen et al, 2002b) and water
electrolysis for hydrogen production (Choi et al, 2004). Therefore, in the present study, Eq. (3.37) is used for calculating the relationship between the voltage (V) and current density (j). The theoretical j-V characteristic of the electro-flotation cell is compared with the experimental data obtained from Chen et al (2002a). Chen et al (2002a)’s experimental work on electro-flotation of waste water has been selected because the laboratory setup and test procedures are clearly reported, which can facilitate the theoretical simulation. Moreover, the inter electrode gap was reduced to 2 mm, which is quite rare for a conventional electrode system. In Chen et al (2002a)’s experiments, the electrolysis voltage dependence on the current density by a Ti based anode (Ti/IrO$_2$-Sb$_2$O$_5$-SnO$_2$) were measured. As shown in Figure 3.11, the agreement between the simulated electro-flotation cell potential (using Bruggeman Eq.) and the experimental data is very good. On the other hand, the gap between the experimental cell potential and the predicted cell potential without considering the bubble effect (based on Eq. (3.29)) increases with an increase in the current density. The result reveals that Eq. (3.29) (where no bubble effect is considered) cannot predict the electro-flotation cell voltage, especially at a low inter-electrode spacing.

3.3.3 Overpotential in electro-flotation cell

The Activation Overpotentials for the anode and cathode were calculated using Eqs. (3.9) and (3.10), respectively, and shown in Figure 3.12. The Anode activation overpotential is obviously higher than that of the cathode due to the lower exchange current density of Ti/IrO$_2$-Ta$_2$O$_5$ anode compared to that of SS 316. It should be noted that the activation loss in the present study was assumed to occur at the electrode/electrolyte interface. In an actual electro-flotation cell, the thickness of the electrode does have an effect of the activation loss (Chan et al, 2001), which is ignored in the present study. Anode concentration
overpotentials and cathode concentration overpotentials are calculated using Eqs. (3.19) and (3.27) respectively. As seen in Figure (3.13), the cathode concentration overpotential is higher than that of the anode concentration overpotential, which indicates that the concentration gradient of OH\(^-\) in the cathode diffusion layer is higher than that of the H\(^+\) gradient in the anode diffusion layer under the pH range (6 to 9) studied in the present study.

The anode and cathode overpotentials (activation + concentration) were calculated by using Eqs. (3.38) and (3.39) respectively. As shown in Figures (3.14) and (3.15) the difference between the experimental overpotential and the theoretical overpotential is up to 10 % for both anode and cathode. At a low current density (less than 40 A/m\(^2\)), the difference between the experimental overpotential and the theoretical overpotential were almost insignificant which increased with an increase of current density. A similar trend was observed by Haupin (1971). This may be attributed to the fact that the available electrode surface area is reduced due to presence of bubbles at higher current density.

Overpotentials at anode and cathode have significant contribution to the total cell voltage. However the contribution at the anode and cathode, respectively, varies under different operating conditions. For a current density of 150 A/m\(^2\), the anode, cathode and ohmic overpotentials were calculated by using the model equations for different inter-electrode spacing (2 to 100 mm) and different electrical conductivities (0.5 ms/cm to 15 ms/cm). It is found that the anode overpotential contributes in the range of 0.15 % to 20.16 % and the cathode overpotential contributes in the range of 0.13% to 17.76% of the total electro-flotation cell voltage. Figure 3.16 shows that the highest contribution of the anode and cathode overpotentials on the total cell potential observed at low inter-electrode spacing (2
mm) and high conductivity (15 ms/cm). On the contrary, at a high inter electrode spacing (100 mm) and low conductivity (0.5 ms/cm) the relative contribution of the anode and cathode overpotential is almost negligible (as low as 0.13%).

### 3.4 Summary

An electrochemical model is developed to represent the relationship between the total cell voltage and variables such as the equilibrium potential difference for water split, anode activation overpotential, anode concentration overpotential, cathode activation overpotential, cathode concentration overpotential and ohmic overpotential in an electro flotation process, based on the Nernst equation, Tafel equation, Fick’s model, and Ohm’s law. The simulation results are compared with experimental data of the present study as well as data obtained from the literature, and good agreement was found. Therefore, the model can be used to calculate the total required electrolysis voltage for an electro-flotation cell under different operating conditions. The effect of bubbles between electrodes on the electrolysis voltage of electro-flotation is investigated. The Bubble fractions between anode and cathode were estimated to be 30% to 35%, which significantly increase the cell resistance and hence the overall cell potential.

The Overpotentials at anode and cathode have significant contribution to the total cell voltage. However the relative contribution on the anode and cathode varies under different operating conditions. The anode and cathode overpotentials were measured experimentally and the results were within 10% of that predicted by the model equations. Among all the approaches used to measure the cell resistance in the present study, the Bruggeman Eq. (3.34) is found to be best suited for electro flotation.
3.5 References:


Elmore, F.E., 1905. A process for separating certain constituents of subdivided ores and like substances, and apparatus therefore, British patent 13,578.


Figure 3.1: A typical potential distribution between electrodes
Figure 3.2 Concentration variation of $H^+$ and $OH^-$ near Anode (left) and Cathode (right) (based on (Chen et al, 2002b))
Figure 3.3: A simplistic model of bubble layer in the electro-flotation cell between anode and cathode and anode.
Figure 3.4 XPS analysis Ti plate
Figure 3.5: Voltage measurement points (a) photo (b) schematic diagram
Figure 3.6: Calculation of experimental anode, cathode and ohmic over-potential
Figure 3.7 Effect of bubbles on ohmic overpotential as a function of current density
Figure 3.8  Effect on bubbles on resistivity as a function of inter-electrode spacing
Figure 3.9 A comparison of equations to predict resistance of electro-flotation cell as a function of inter-electrode spacing
Figure 3.10 Comparison between predictions by Equation 3 and the experimental values
Figure 3.11 Comparison between theoretical and experimental results
Figure 3.12 Activation over-potential versus current density
Figure 3.13 Concentration over-potential versus current density
Figure 3.14 Comparison between theoretical and experimental anode overpotential
Figure 3.15 Comparison between theoretical and experimental cathode overpotential
Figure 3.16 Relative contributions of different components on total cell voltage
CHAPTER 4

BUBBLE SIZE DISTRIBUTION IN LABORATORY SCALE ELECTRO-FLOTATION STUDY

4 Introduction

Flotation is a unit operation for solid-liquid separation by introducing fine gas bubbles into the liquid phase. Its separation efficiency is largely dependent on the size of the bubbles formed. Bennet et al. (1958) first reported the effect of bubble size and found that smaller bubbles were more effective in the flotation of coal particles. Other studies also confirmed the role of bubble size in fine particle flotation (e.g. Ahmed and Jameson, 1985; Lee, 1969). Sarker et al (2010) stated that the conventional mechanically agitated and sparged column flotation cells produce air bubbles that are too large for the flotation of fine particles. Ahmed and Jameson (1985) found that bubble size has a strong influence on the flotation rate constant (K). The first order kinetic constant varies as a function of reciprocal of bubble diameters (d_b): d_b^{-3} at quiescent conditions (Yoon, 2000) and approximately vary as d_b^{-1.5} under turbulent conditions (Heiskanen, 2000). Electro-flotation (EF) has the advantage of generating finely dispersed hydrogen and oxygen bubbles (Bande et al, 2008). Moreover, the bubble sizes and concentration can be controlled by the current density, hence enhance the probabilities of bubble-particle collisions. Electrochemical reactions due to electrolysis are well understood, i.e. (Sarkar, 2012):

\[ 2H_2O \rightarrow O_2 + 4H^+ + 4e \]  \hspace{1cm} (4.1)
\[4H^+ + 4e \rightarrow 2H_2\]

(4.2)

The physical procedure of bubbles formation can be divided into three phases: nucleation, growth and detachment (Vogt, 1983). When the molecular oxygen and hydrogen form (as shown in Eqs. 4.1 and 4.2), they moved away from the anode and cathode respectively. Consequently, an excessive concentration gradient of dissolved oxygen and hydrogen builds up near anode and cathode, respectively. If the concentration gradient exceeds a threshold, nuclei at the electrode surface become active, and oxygen and hydrogen are transformed into the gaseous phase near the anode and cathode, respectively (Vogt, 1983). Gas bubbles grow by the internal pressure of the bubble (Lumanauw, 2000) as well as mass transfer of dissolved oxygen or hydrogen from the electrodes to the nuclei of the corresponding gas. Five different forces act on a growing bubble. Among them, drag force \((F_d)\) and surface force \((F_s)\) hold the bubble on the electrode surface, whereas liquid inertia force \((F_i)\), pressure force \((F_p)\), and buoyancy force \((F_b)\) pull the bubble away the surface (Lumanauw, 2000). When the sum of \(F_i\), \(F_p\) and \(F_b\) exceeds \(F_d\) and \(F_s\), bubbles depart from the electrode. The bubbles continue to absorb gas from the supersaturated water when rising from the electrode after being detached from the electrode (Vogt, 1983) and reaches its maximum size at around 1 mm from the electrode surface (Sarkar et al, 2010). Many researchers worked on determination of bubble size at the time of departure (e.g. Al-Hayes and Winterton, 1981), however no satisfactory theory has yet been developed (Lumanauw, 2000).
Bennett et al. (1958) showed that the flotation rate can be increased not only by reducing the bubble size but also by generating more bubbles. The higher bubble flux provides more opportunity for collisions. In an EF process, the bubble fluxes, i.e. the oxygen and hydrogen can be controlled by the current according to the Faraday’s law (Chen and Chen, 2010):

\[ Q_O = \frac{IV_O}{F n_O} \]  
\[ Q_H = \frac{IV_O}{F n_H} \]  

Where, \( Q_O \) (L/sec) and \( Q_H \) (L/sec) are the generating rates of \( O_2 \) and \( H_2 \) respectively, at the normal state, \( V_0 \) is the molar volume of gases at the normal state (22.4L/mol); \( F \) is the Faraday’s constant (96,500 C/mol of electrons); \( I \) is the current (Amp), \( n_O \) is the electrons transfer number of \( O_2 \) (4 mol electrons per mole of \( O_2 \)) and \( n_H \) is the electrons transfer number of \( H_2 \) (2 mol electrons per mole of \( H_2 \)). Substituting the values of \( V_0 \), \( F \), \( n_O \) and \( n_H \), Eq. (4.3) and Eq (4.4) can be re-written as (Chen and Chen, 2010):

\[ Q_O = 0.58 \times 10^{-4} I \]  
\[ Q_H = 1.16 \times 10^{-4} I \]  

Total number of oxygen and hydrogen bubbles generate in an EF cell per unit time can be approximated by Eq. (4.7) and Eq. (4.8) respectively:

\[ N_O = f_O \frac{Q_O}{\pi d_{b/O}^2/6} \]  
\[ N_H = f_H \frac{Q_H}{\pi d_{b/H}^2/6} \]
Where, \( d_{b/O} \) and \( d_{b/H} \) are the mean bubble dia of \( O_2 \) and \( H_2 \) respectively, \( f_O \) and \( f_H \) are the fraction of total \( O_2 \) and \( H_2 \) transformed into bubbles. The procedure for determination of \( f_O \) and \( f_H \) has been described in detail elsewhere (e.g. Vogt, 1984).

The size of the desired bubble generation can be controlled by the current density, pH and by choosing various metal electrodes with various surface geometries (Raju and Khangaonkar, 1984). Although bubble size is a key parameter in EF, bubble size has rarely been studied in lab scale flotation cells. Among the limited number of studies, there is still contradiction among the researchers regarding the effect of current density on bubble size. For example, Ketar et al. (1991) and Khosla et al. (1991) showed that with an increase in the current density, the bubble diameter decreases. However, Sides (1986) and Landolt et al. (1970) reported an opposite effect due to the bubble coalescence at higher current densities. The study of Burns et al. (1997) suggested that there is no clear trend of bubble diameters as a function of current density at low values (40-210 A/m²). Lumanauw (2000) concluded that the mean bubble size increases with current density for smooth surface electrodes, whereas the opposite trend is observed for rough-surface electrodes (Liuyi et al., 2014). It is understandable that the inconsistency among the researches on measuring the bubble size in open literature is a result of different testing methods, electrode materials, surface areas and smoothness, as well as the medium conditions such as electrolyte and pH.

The dimensionally stable anodes (DSA) invented by Beer (1972) in the late 1960s are the most important anodes in EF due to their corrosion resistance properties and long service life. However, the effect of DSA anode on size of oxygen bubble has not yet been investigated. Furthermore, there is still contradiction among the researchers regarding the
bubble size distribution in EF. Burn et al (1997) assumed the normal distribution to calculate the bubble sample size. On the other hand, Fukui and Yuu (1985) expressed the bubble size distribution as the log normal distribution.

The uncertainty in influencing factors mentioned above has made it difficult to effectively design efficient EF systems for fine particle recovery (Sarkar, 2010). This study was aimed at reducing the uncertainty by investigating the size of hydrogen and oxygen bubbles produced from Stainless steel (SS 316) and Ti-IrO₂ (DSA) electrodes as a function of current density, pH, electrode geometries, KNO₃ concentration and frother concentration. Furthermore, four mathematical distributions (normal, log-normal, Weibull (Rosin–Rammler) and gamma distributions) are fitted to the experimental data to assess the mathematic distributions of bubble sizes in an EF cell.

4.1 Experimental setup

In this study, the qualitative and quantitative observations of oxygen and hydrogen bubble evolution in EF have are made using image analysis. The experimental setup was consisted of an electro flotation cell, made of Plexi glass, a DC power supply, a light source, and a high-speed camera, as shown in Figure 4.1. Iridium dioxide coated titanium plate (TP), known as DSA, was used as the anode and stainless steel SS 316 plate (SP) was selected as the cathode. In a few experiments, stainless steel mesh (SM) with wire dia of 1.6 mm and aperture of 6.87 mm was also used to investigate the effect of the geometry on bubble size. Details of the electrode configuration as well as experimental conditions are listed in Table 4.1. The electrodes were attached near the bottom of the cell, with a separation of 15 cm between the anode and cathode, and connected to a DC power supply. KNO₃ was used
as the supporting electrolyte to provide ions for conduction. Once the power was turned on, hydrogen and oxygen bubbles were produced from the cathode and anode, respectively. The hydrogen and oxygen bubbles were observed through the camera lens, which was placed (see Figure 4.1) in such a way that it is focused on the bottom electrode. Therefore, there was no mixing of H₂ and O₂ bubbles during capturing photos. Images of the bubbles were taken using an EOS Canon 60D with high-resolution (5184 pixels × 3456 pixels). Magnifications were made using a Raynox DCR-250 macro lens in conjunction with 18 to 135 mm of Canon Zoom lens. The bubbles were illuminated from behind using a LED light source. The shutter speed of the camera was set to 1600 per second, with f-number 5.6, to provide a clear image of fast moving bubbles. The bubble evolution images was taken at various conditions including different current densities (10 to 150 A/m²), water pH (2 to 12), electrode materials (either steel or Ti/IrO₂ as anodes), KNO₃ concentration (0.1 M to 0.5 M) and frother (tenafroth 250) concentration (10 to 30 mg/L). The resolution of each image was calibrated by taking photo of a scale located in the plane of the rising bubbles. The images were examined using Imagej software to obtain the bubble diameter. All experiments were performed using de-ionized water. A typical image of the bubbles is shown in Figure 4.2.

4.2 Bubble size distribution

The size distribution of bubbles is the key in flotation as only bubbles of certain size serve a useful purpose (Ben-Yosef et al, 1974). Therefore, it is the key to know the exact bubble size distribution in designing a flotation cell. Tavlarides and Stamatoudis (1981) and Pacek et al. (1998) reported that the log-normal distribution describes droplet size distributions in liquid–liquid dispersions. Zhang et al (2008) suggested that most small rising bubble size
distributions are well characterized by log-normal or gamma distributions in a gas–liquid and gas–liquid–solid slurry bubble column reactor. On the other hand, Biswal et al (2008) found that the bubble size distribution in the flotation follows the Rosin-Rommler equation. Therefore, in the present study, normal, log-normal, Weibull (Rosin–Rammler) and gamma distributions were fitted to the experimental data. The Normal (Gaussian) distribution is characterized by a bell-shaped curve that is symmetrical around the mean; the log-normal distribution is a probability distribution of a random variable whose logarithm is normally distributed (Buzsáki and Mizuseki, 2014). Alternatively, the Weibull and gamma distributions are described by the shape, scale, and threshold parameters (Silva and Lisboa 2007). The probability distribution functions of those four distributions have been described in detail elsewhere (Fatima and Fortes, 1987; Silva and Lisboa 2007).

The Anderson-Darling (AD) test has been used to compare these distributions to identify the best fit for the bubble size distribution in EF (Stephens, 1974). In this study, the experimental data were processed for the AD test by statistical software MINITAB 15. In an Anderson-Darling test, if the P-value is lower than 0.05 at the confidence interval of 95%, the data do not follow the specified distribution. The smallest Anderson-Darling (AD) values identify the closest fit distribution.

4.3 Result and discussions

The AD values of different bubble size distributions of EF are presented in Table 4.2. As seen the log-normal and gamma distributions are fairly similar according to the values of AD. Silva and Lisboa (2007) also stated that the log normal and gamma distributions are similar in shape for the same coefficient and are widely used for describing positively
skewed data. The differences between the gamma and log-normal distribution become most significant in their tail behavior (Henk, 2003, Silva and Lisboa 2007). The logarithm of gamma distribution has more of a tail on the left, and less of a tail on the right. On the other hand, the log-normal distribution is symmetric with a heavier right tail.

It is observed that the AD values for the log-normal and gamma distributions are close (Table 4.2). However, a good argument in favor of the log-normal distribution is presented based on the lower AD value. Moreover, since the P-values according to the AD log-normality test for bubbles size distributions are consistently higher than 0.05, it can be concluded that log-normality distribution is valid for bubble size distribution in the EF cell (Alam et al, 2011). On the other hand, the P-values for the normal, and Weibull (Rosin–Rammler) distributions are very low with high AD values. Therefore, bubbles size distributions in EF do not fit well by either normal or Weibull distribution. The individual probability plot for normal, log-normal, Weibull (Rosin–Rammler) and gamma distributions also shows that in the log-normal distribution, the data points approximately follow a straight line with the highest P-value. Example of this probability plot is shown in Figure 4.3 based on the result of Exp. no. 10. Therefore, it can be concluded that the experimental bubble size distributions were satisfactorily represented by the log-normal distribution, in which the probability density function of bubble size \(d_i\) can be expressed as (Fatima and Fortes, 1988):

\[
P (d_i) = \frac{1}{d_i \sigma \sqrt{2\pi}} \exp \left[ \frac{- (\ln d_i - \bar{d}_b)^2}{2(\sigma)^2} \right]
\]  

(4.9)

Where, \(\sigma\) and \(\bar{d}_b\) are the standard deviation and arithmetic mean of \(\ln d_i\). Upon integration of Eq. (4.9), the cumulative distribution function can be expressed as
\[ D(d_i) = \frac{1}{2} [1 + \text{erf} \left( \frac{\ln d_i - d_b}{\sigma \sqrt{2}} \right) ] \]  

(4.10)

The experimental results of bubble size distribution will be discussed in the following sections according to the simulated log-normal distributions (based on Eq. (4.9) and (4.10)). In addition, the quality of data fitting to the log-normal function is shown graphically in Figures 4.5 (a), 4.6(a), 4.8(a), 4.9(a), 4.12(a), 4.13(a), 4.15(a), 4.16(a), 4.18(a) and 4.20(a).

### 4.3.1 Effect of pH

To assess the effect of pH on bubble size of EF, a series of batch tests were performed (Exp no 1-6). The current density was kept constant throughout the series while the water pH (2, 7 and 12) was varied. Figure 4.4 shows that the pH of the electrolyte medium can significantly affect the mean bubble size of both hydrogen and oxygen bubbles. The smaller mean bubble size of hydrogen (33.9 µm) was obtained under near neutral pH values, whereas the mean bubble size of hydrogen in strongly acidic (pH = 2) and alkaline (pH = 12) media are larger, i.e. 65 and 50 µm, respectively. On the other hand, oxygen formed on a Ti-IrO\(_2\) plate attained a mean bubble size of 32.7 µm in an acid medium and increased with pH increase. The trend is consistent with that of previous studies (e.g. Raju and Khangaonkar, 1984; Glembotsky et al. 1973; Brandon and Kelsall, 1985). This trend can be described by Eq. (4.8) which suggests that if the current density is constant (i.e. the generating rate of O\(_2\) and H\(_2\) is constant) bubble dia is inversely proportional to the total number of bubbles generate per unit time. Generally, a lower number of H\(_2\) bubbles are observed at extremely low and high pH compared to that at neutral pH (Carlos, 2010). Therefore, more nucleation sites become active on the cathode surface at neutral pH for.
which a decrease in H₂ bubble diameter occurs at neutral pH. For similar reason, smaller O₂ bubbles are observed at low pH. It is also observed that when the pH is close to 6.0 the mean bubble sizes of H₂ and O₂ come very close to each other (Figure 4.4) which is consistent with the result of Raju and Khangaonkar (1984).

Figure 4.5 shows the simulated log-normal distribution of O₂ bubble size at different pH. As can be seen from the distribution curve, the amount of fine bubbles increased as the pH decreased. Several researchers (e.g. Ketkar et al 1991) have stated that one of the advantages of EF is to produce uniform bubble size. However Figure 4.5 shows that a wide range of bubbles was produced with a difference of as much as 50 µm at pH 7 and pH 12. The variations in H₂ bubble size are illustrated in Figure 4.6. As seen in the figure, the finer bubbles are generated at pH 7. On the other hand, at pH 2, H₂ bubbles have a wider range. Grau and Heiskanen (2005) stated that a broad range of bubble sizes might have a positive effect on the flotation of coarse particles. In summary, this study reveals that the desired bubble size and distribution can be manipulated by varying the pH value of the medium in EF.

4.3.2 Effect of current density

The Current density is the most important parameter in an EF process. Effects of the current densities on the bubble size and distributions are shown in Figures 4.7-4.9. The current density in the experiments varied between 10 and 150 A/m² while the other conditions were kept constant. Bubbles generated at 10 A/m² are comparatively large, and does not show any sign of coalesce. On the other hand, at the current density 150 A/m², the amount of bubbles significantly increases, as described in the Faraday's law, and the coalesce of
bubbles is clearly observed (Figure 4.2). Figure 4.7 shows that the mean bubble size of both O\textsubscript{2} and H\textsubscript{2} decreases with the increase in the current density up to 100 A/m\textsuperscript{2}. It is well established that the diameter of bubbles at the time of departure from the electrode decreases as the current density is increased (Vogt, 1989). Because as current density increases, more nucleation sites become active on the electrode surface and lead to generate smaller bubbles (Lumanauw, 2000). However it is noteworthy to mention here that the findings reviewed by Vogt (1989) or experiments conducted by Lumanauw (2000) strictly refers to the diameter at detachment from an electrode; not for freely moving bubbles. In the present study, a further increase in the current density above 100 A/m\textsuperscript{2} causes an increase in the size of free moving bubbles. This is attributed to the fact that at higher current densities, a large number of bubbles are produced, which facilitates the coalescence process and form large bubbles.

Figure 4.8 shows the bubble size distribution of O\textsubscript{2} for different current densities. As seen in the figure, the increase in current density has a strong influence on the bubble size distribution of O\textsubscript{2}. It was found that finer bubbles are produced at 100 A/m\textsuperscript{2}. The variations in H\textsubscript{2} bubble size are illustrated in Figure 4.9. As seen, the bubble-size distribution was shifted towards smaller bubble size as the current density was increased up to 100 A/m\textsuperscript{2} and again was shifted towards larger bubble size as the current density was increased to 150 A/m\textsuperscript{2}.

As mention earlier that EF can control the number of bubbles by changing the current density; the relationship between the number of bubbles and current density was determined for Exp. nos. 2, 5 and 7-14. The amount of both oxygen and hydrogen bubbles were counted under the same area (1 cm\textsuperscript{2}) of different images for various current densities.
The results are shown in Figure 4.10. The linear relationship between the current density and the number of bubbles is in agreement with Eqs. (4.5) and (4.6). Moreover, it is noteworthy to mention here that the number of hydrogen bubbles are almost twice than that of oxygen bubbles under the same current density.

4.3.3 Effect of frother

Frothers are widely used in flotation to assist generation of small bubbles. The major function of the frother is to conserve the size of bubble by preventing coalescence (Cho and Laskowski, 2002). Moreover, recent studies (Kracht and Finch, 2009) have shown that frothers also help to break down bubbles, thus reducing bubble sizes. Although the frother plays an important role in froth flotation (Grau and Laskowski, 2006), the use of frother in EF has not yet been extensively reported in open literature. To assess the effect of frother (tennafroth 250) on bubble size of EF, a series of batch flotation tests were performed (Exp nos. 25-30). The frother concentration in the experiments varied between 10 mg/L and 30 mg/L while the other conditions were kept constant. The measured bubble size vs frother concentration is shown in Figure 4.11. As seen the bubble size decreased with increasing frother dosage up to 20 mg/L, above which further increase of the frother concentration does not affect the bubble size. Grau et al (2005) defined this point as the critical coalescence concentration (CCC) of frother. Cho and Laskowski (2002) showed that the coalescence is completely prohibited at the frother concentrations exceeding CCC values. It is clear from Figure 4.11 that at frother dosages exceeding the CCC value of 20 mg/L for both O₂ and H₂ bubbles, the conditions in the cell can be defined as non-coalescing. Figure 4.12 shows the O₂ bubble size distributions measured under different frother concentrations. As seen in the Figure (4.12), the amount of fine bubbles increased notably
as the concentration of frother increased. The variations in H\textsubscript{2} bubble size are illustrated in Fig 4.13. It is found that the mean size of H\textsubscript{2} decreased, and the number of finer bubbles increased significantly as the concentration of frother increased.

4.3.4 Effect of Ionic strength

Dai et al. (2007) found that bubble size decreases with increasing the ionic strength of the electrolyte solution. However Liuyi et al (2014) reported the opposite trend, which was attributed to agglomeration of bubbles. Burns et al. (1997) suggested that there is no clear trend of bubble diameters as a function of the ionic strength. Therefore, in the present study, the effect of ionic strength (by adding KNO\textsubscript{3}) on the bubble size was investigated in a series of experiments. The Current density and pH were kept constant throughout the tests while the concentration of KNO\textsubscript{3} was varied between 0.1 M and 0.5 M, under the same electrode configuration. Figure 4.14 shows a slight decrease in the bubble size with increasing ionic strength, which supports the findings of Dai et al (2007). The findings might be explained by two previous studies conducted by M\'ymicci and Nicoderno (1967) and Ziemenski and Whittemore (1971). Ziemenski and Whittemore (1971) found that adding salt in solution increase the viscosity of the electrolyte and hence increase the rigidity of the surface films of the bubbles so that the coalescence is more difficult. Furthermore, M\'ymicci, and Nicoderno (1967) suggested that adding salt would increase the electric repulsive forces between bubbles for their high surface potential, which would also help to avoid collision. Figures 4.15 and 4.16 show the bubble size distribution of O\textsubscript{2} and H\textsubscript{2} respectively for different KNO\textsubscript{3} concentrations. It was found that the bubble-size distribution was shifted slightly towards the smaller sizes as the concentration of KNO\textsubscript{3} was increased for both O\textsubscript{2}
and H₂. Therefore, it can be concluded that KNO₃ would reduce bubble sizes, however it is to less extent comparing to the frother.

4.3.5 Effect of electrode materials and geometry

The mean H₂ bubble sizes as a function of current density (from 10 to 150 A/m²) for the SS plate and SS mesh electrode are shown in Figure 4.17. The SS mesh electrodes produce the largest bubble (101.5 μm) diameter within the current density ranges studied. Bubbles generated from the SS mesh might have a larger contact angle and consequently produce longer bubble foot perimeter that holds the bigger bubble on the surface (Lumanauw, 2000). Figure 4.18 shows the H₂ bubble size distributions for the SS plate and SS mesh electrode. It is found that SS plate produces more finer bubbles with compared to that of SS mesh electrodes.

The mean bubble measurements as a function of current density (10 to 150 A/m²) for the SS 316 plate and Ti/IrO₂ plate electrode are shown in Figure 4.19. As seen in the figure, the Ti/IrO₂ plate produces comparatively smaller O₂ bubbles under the same operating condition. The difference in wettability (related to the adhesion force) of the two materials may have impact on the bubble size (Ibl, and Venczel, 1970). Figure 4.20 compares the bubble size distributions for the SS 316 plate and Ti/IrO₂ plate electrode. It is found that the Ti/IrO₂ plate produces finer bubbles compared to that of the SS plate.
4.4 Summary

The following conclusions are reached based on the present study:

- The experimental data obtained from the tests conducted in the lab scale EF cells were well represented by the log-normal distribution.

- The water pH has significant effect on bubble sizes. The smaller bubbles of H\textsubscript{2} at the cathode were observed at near neutral pH values, whereas smaller bubbles of O\textsubscript{2} at the anode were observed in low pH water.

- The Current density has significant effect on the bubble size. The mean bubble size decreases with the increase in the current density up to a threshold value of 100 A/m\textsuperscript{2}. Further increase in the current density causes an increase in bubble sizes, which is attributed to the coalescence of free moving bubbles.

- The study on the frother (tennafroth 250) shows that with increasing frother concentration, the bubble size decreased until a critical coalescence concentration (CCC) was reached. At concentrations above CCC, no further changes in the bubble size were observed.

- A slight decrease in the bubble size was observed with the increase of ionic strength (by adding KNO\textsubscript{3}).

- It is found that when used as the anode, the Ti/IrO\textsubscript{2} plate produces finer O\textsubscript{2} bubbles than the stainless steel SS 316 plate.
4.5 References


Lumanauw, D. 2000. Hydrogen bubble characterization in alkaline water electrolysis, thesis of Master of Applied Science, Department of Metallurgy and Materials Science, University of Toronto


Silva, EL and Lisboa, P. 2007. Analysis of the characteristic features of the density functions for gamma, Weibull and log-normal distributions through RBF network pruning with QLP Proceedings of the 6th WSEAS Int. Conf. on Artificial Intelligence, Knowledge Engineering and Data Bases, Corfu Island, Greece, February 16-19, 2007


### TABLES

**Table 4.1 Experimental Condition**

<table>
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<td>14</td>
<td>1.057 (P = 0.008)</td>
<td>0.441 (P = 0.280)</td>
<td>1.476 (P &lt; 0.01)</td>
<td>0.608 (P = 0.121)</td>
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<td>0.383 (P = 0.381)</td>
<td>1.042 (P &lt; 0.010)</td>
<td>0.477 (P = 0.243)</td>
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<td>0.278 (P = 0.635)</td>
<td>0.338 (P &gt; 0.250)</td>
<td>0.239 (P &gt; 0.250)</td>
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Figure 4.1 Schematic diagram of the Experimental set-up
Bubble coalescence at higher current density

Bigger bubble forms from coalescence of two bubbles

**Figure 4.2** Bubble coalescence at high current density
Figure 4.3 probability plot for different types of distribution
Figure 4.4 Effect of pH on bubble size

pH at which the mean size of H₂ and O₂ are approximately equal
Figure 4.5: Bubble size distribution of O₂ measured at different pH: (a) comparison of experimental data with the simulated cumulative log-normal distribution (b) Simulated log-normal distribution of bubbles
Figure 4.6: Bubble size distribution of H$_2$ measured at different pH: (a) comparison of experimental data with the simulated cumulative log-normal distribution (b) Simulated log-normal distribution of bubbles
Figure 4.7 Effect of current density on mean bubble size
Figure 4.8: Bubble size distribution of O$_2$ measured at different Current density: (a) comparison of experimental data with the simulated cumulative log-normal distribution (b) Simulated log-normal distribution of bubbles
Figure 4.9: Bubble size distribution of H$_2$ measured at different Current density: (a) comparison of experimental data with the simulated cumulative log-normal distribution (b) Simulated log-normal distribution of bubbles
Figure 4.10 Effect of current density on number of bubbles/cm$^2$: (a) O$_2$ bubbles (b) H$_2$ bubbles
Figure 4.11 Effect of Frother (tennafroth 250) concentration on mean bubble size
Figure 4.12: Bubble size distribution of O₂ measured at different frother concentration: (a) comparison of experimental data with the simulated cumulative log-normal distribution (b) Simulated log-normal distribution of bubbles
Figure 4.13: Bubble size distribution of H₂ measured at different frother concentration: (a) comparison of experimental data with the simulated cumulative log-normal distribution (b) Simulated log-normal distribution of bubbles
Figure 4.14 Effect of KNO₃ concentration on mean bubble size
Figure 4.15: Bubble size distribution of O₂ measured at different KNO₃ concentration: (a) comparison of experimental data with the simulated cumulative log-normal distribution (b) Simulated log-normal distribution of bubbles
Figure 4.16: Bubble size distribution of H₂ measured at different KNO₃ concentration: (a) comparison of experimental data with the simulated cumulative log-normal distribution (b) Simulated log-normal distribution of bubbles
Figure 4.17 Effect of geometry of Cathode on mean bubble size
Figure 4.18: Bubble size distribution of H$_2$ measured for SS plate and Mesh: (a) comparison of experimental data with the simulated cumulative log-normal distribution (b) Simulated log-normal distribution of bubbles
**Figure 4.19** Effect of Anode materials on mean bubble size

- **SS 316**
- **Ti/IrO2**
Figure 4.20: Bubble size distribution of $O_2$ measured for Ti/IrO$_2$ and SS 316 plate: (a) comparison of experimental data with the simulated cumulative log-normal distribution (b) Simulated log-normal distribution of bubbles
CHAPTER 5
REMOVAL OF BITUMEN FROM MATURE OIL SANDS TAILINGS SLURRIES
BY ELECTRO-FLOTATION

5 Introduction

The oil sands deposit in northern Alberta, Canada, is estimated to contain 174 billion barrels of bitumen (Alberta Energy and Utilities Board 2005). The Canadian oil sands industries withdraw an average of 3 barrels of freshwater for every barrel of oil produced (Allen, 2008). The resulting process water of the oil sands mining operation is discharged in large tailings ponds. Allen (2008) has identified some target pollutants in the tailings ponds’ water, which should be reduced to an allowable level so that the tailings can be used directly in the reclamation process (Elliott et al 2010). Residual bitumen, one of the target pollutants poses a hazard to aquatic biota, and its biodegradation could be a source of Naphthenic Acid (Quagraine et al. 2005). Bitumen would disturb aquatic communities in reclamation ponds, and contribute to the fouling of advanced treatment technologies. Bitumen concentrations (measured as oil and grease) in tailings ponds water have been at least 2.5 to 9 fold higher than the EPEA maximum discharge limit of 10 mg/L, thus up to 90% removal may be required (Allen, 2008).

Flotation has been recognized as the most economical way to separate bitumen since it has a similar density to water (Masliyah et al 2004; Bichard, 1987). During extraction of bitumen, caustic or sodium hydroxide is added to increase oil sands slurry pH, making solids and bitumen more negatively charged, thereby helping bitumen liberation from sand
grains (Lau et al 2013, Zhou et al, 2010, Dai, and Chung, 1995). Therefore, the pH of MFT slurries often ranges from 8 to 9, which makes the bitumen surface fairly hydrophobic with contact angles greater than 70 degrees (Zhou, 2002). In addition, the caustic environment of the slurry induces ionization of natural surfactants (carboxylates and sulphonates/sulphates) for which no frother is needed in bitumen flotation for stabilizing bubbles (Zhou et al, 2010). Therefore, flotation can be considered as the most viable technology to remove bitumen from tailings pond.

For flotation of oil, fine gas bubbles are introduced into the slurry. The bubbles attach to the bitumen and the buoyancy lifts bitumen to the surface, which is then collected by skimming. Gas bubbles can be produced through many methods, for example, dissolved air-flotation, electrostatic spraying of air, and electrolysis, which is the principle of electro-flotation (Burns, 1997). Conventional air flotation generates large bubbles, ranging in sizes from 600 to 2000 μm (Wills, 1997). Some spargers can produce medium bubble sizes from 100 to 600 μm (Montes-Atenas et al, 2010). Guoxing et al (2004) reported from an experimental study that bubbles sizes lower than 120 μm are favorable for flotation of bitumen. Electro flotation (EF) is capable of producing hydrogen and oxygen bubbles consistently smaller than 120 μm from water electrolysis. In EF, an electrolyte solution is brought between two electrodes, and a direct current (dc) is passing through from the positive pole (anode) to the negative pole (cathode). As a result of electrolysis reactions, hydrogen and oxygen are formed at cathode and anode, respectively, in the form of gas bubbles. The redox reactions at the electrodes can be expressed as (Chen and Chen, 2010):
At the anode,

\[ 2H_2O \rightarrow O_2 + 4H^+ + 4e \]  \hspace{1cm} (5.1)

At the cathode,

\[ 4H^+ + 4e \rightarrow 2H_2 \]  \hspace{1cm} (5.2)

The EF technique is versatile and competitive with other flotation techniques, such as dissolved and dispersed air flotation (Burns et al, 1997). EF units are small, compact and require lower maintenance and running costs than other flotation units (Kolesnikov, 1994). In general, EF has three principle features that are advantageous comparing to other flotation techniques, (Bande et al, 2008): i.e. 1. Extremely fine dispersed gas bubbles those are uniform in sizes. This increases the surface area of contact between oil drops and gas bubbles. 2. A specific gas bubble concentration and size can be generated by controlling the current density, thereby increasing the probabilities of bubble and oil drop collisions. 3. The process can be optimized by the selection of an appropriate electrode surface and solution conditions. In addition, it can achieve separation in much shorter retention time compared to that of air flotation (Ibrahim et al, 2001). Applications of EF are especially attractive for separation of oil from oil-water emulsions because of the low density of oil, which has been reported extensively in the literature (Matis and Peleka, 2010, Hosny, 1996, Mansour and Chalbi, 2006, Ibrahim et al. 2001, Vasibenko et al, 1973; Belyacva et al, 1980; Balmer and Foulds 1986; Il’in 2002; Il’in and Sedashova 1999). EF is also successfully implemented for separation of paint solids from automotive assembly paint booths without using any chemical agents or compressed air (Xu and Shang, 2009). EF is
accepted as a cost effective means of treating effluents in Europe, where they compete strongly with established process such as dissolved air flotation (Sarkar, 2012).

The objectives of this study are 1) to study the effect of EF for removal of bitumen from oil sand tailings slurry; the target is to reduce the bitumen concentration to below the EPEA maximum discharge limit (10 mg/L); and 2) to investigate the EF performance related to variations of operating parameters (Current density, pH, bitumen concentration and NaCl dosage).

5.1 Experimental

5.1.1 Mature fine tailings slurry

The flotation experiments were carried out using MFT samples obtained from a tailings disposal pond in Fort McMurray, Alberta, Canada. The properties of Mature Fine Tailings (MFT) have been studied (e.g. Alam et al, 2014; Guo, 2012), with a summary presented in Table 5.1. The tailings can be characterized as MH according to the Unified Soil Classification system (ASTM D2487), with about 80% silt-sized grains, and 20% clay sized grains, 54.42% liquid limit, 36.04% plastic limit and plasticity index of 18.38. Mineralogical analysis using X-ray diffractometry revealed that the mature fine oil sands tailings contain 26-30 % quartz (SiO₂), 40-50% illite (KAl₂Si₃O₁₀(OH)₂), 11-25% kaolinite (Al₂Si₂O₅(OH)₄) and trace amount of goethite (FeO(OH)) and biotite (K(Mg,Fe)₃(AlSi₃O₁₀)(F,OH)₂) (Guo, 2012). The water content of the tailings as received was found in the range of 158 % to 171%. The specific gravity of the sample was between 2.5-2.6. The dry density and void ratio of the sample were 0.49 g/cm³ and 4.26 respectively. The organic matter of the sample was found in the range of 14.5 to 18%, of which a
significant portion is bitumen. The pH of the tailings sample was 8.5, which makes the slurry favorable to flotation of bitumen due to its effects on the physical properties of the system, such as interfacial tension (Drelich, 2008) and electric surface potential (Czarnecki et al, 2005).

Oil sands slurry was synthesized by mixing MFT with hot distilled water (80ºC) for 3 hours. The slurry was further diluted before the EF treatment by mixing with distilled water for another 3 hours to achieve the desired concentrations of bitumen in the slurry to replicate the actual tailings pond water.

5.1.2 Flotation

The laboratory scale studies were carried out in a flotation cell, as shown in Figure 5.1. The cell has a volume of 4.5 L, with the length 22 cm at the top and 15.4 cm at the bottom, the width 16.7 cm, and the height 25.2 cm. The cathode was placed horizontally at the top of the anode, which is made of a stainless steel mesh (SS 316), an Iridium dioxide coated titanium (Ti) mesh was used the anode. The spacing between the electrodes was 15 mm. This electrode configuration has shown to be effective for quick dispersion of small gas bubbles (Xu and Shang, 2009). The dc current for the circuit was maintained by a DC power supply (HP 6545A). The experiments were carried out under various operating conditions, including current density (50 A/m² to 300 A/m²), bitumen concentration (22.48 mg/L to 314.72 mg/L), pH (3.3 to 10.68) and NaCl dosage (17.5 g/kg to 70 g/kg) (for adjustment of water electrical conductivity). A summary of the flotation test conditions is presented in Table 5.2. The pH was adjusted to a desired value through HCl or NaOH solutions just before the test. After conditioning the slurry, the DC power was switched on and regulated to a selected current density. The experiments were carried out by stirring
the oil sand slurry at an agitation speed of 175 rpm for the duration of 90 min, during this period the froth was collected. Samples of 10 ml were taken from the supernatant at a depth of 50 mm below the free surface of the flotation cell at 10, 20, 30, 60 and 90 min during each test. The bitumen removal rate, \( R \) (%) from the flotation unit was evaluated by using the following equation:

\[
R \, (\%) = (1 - \frac{C}{C_0}) \times 100
\]  

(5.3)

Where, \( C_0 \) and \( C \) are the initial and final concentrations of bitumen (mg/L) respectively. The concentration of bitumen (as oil and grease) was determined with a FTIR spectrometer (Nicolet 6700) using the wave number of 2920 cm\(^{-1}\) by ASTM D7575 (See appendix B). The oil and grease extractor and the standards were supplied by Orono Spectral Solutions Inc.

5.2 Results and discussions

5.2.1 Flotation Kinetics

Typically the effectiveness of flotation separation is measured by the percentage removal of target pollutant; however the flotation kinetics represents a positive and more accurate understanding for the process (Schuhmann, 1942). The Flotation kinetics studies the deviation of concentration of target species as related to flotation time. Most authors (Alam and Shang, 2012; Hernainz and Calero, 1996) compare the flotation process as analogous to chemical kinetics. The majority of researchers have proposed the first order flotation kinetics for EF of oil (e.g. Hosny, 1996, Mansour and Chalbi, 2006). A generalized expression analogous to chemical kinetics can be used to represent the flotation process:
\[
\frac{dc}{dt} = -KC^n
\]  
(5.4)

Where, \(C\) is the concentration of bitumen at time \(t\), \(K\) is flotation rate constant (min\(^{-1}\)) and \(n\) is the kinetic order. In this study, the first \((n = 1)\) order rate equations have been used to determine flotation rate constant.

In the First Order Rate Equation:

\[
\frac{dc}{dt} = -KC
\]  
(5.5)

Upon integration Eq. 5.5 becomes

\[
\ln \frac{C_0}{C} = Kt
\]  
(5.6)

Eq. (5.6) can be rewritten as

\[
C = C_0e^{-Kt}
\]  
(5.7)

Where, \(C_0\) is the initial concentration of the bitumen in MFT slurries. According to Equation 5.6, \(\ln \frac{C_0}{C}\) and flotation time, \(t\), yield a linear relationship if \(K\) is constant (Alam et al, 2012). An Example of this relationship is shown in Figure 5.2 based on the result of Exp. No. 3. The values of \(K\) and corresponding \(r^2\) values obtained from all experimental data are summarized in Table 5.3. Higher values of \(K\) represent higher removal (R \%) of bitumen. As shown in Table 5.3, the EF of bitumen from oil sand slurries can be represented by the first order flotation kinetics as the values of \(r^2\) is consistently greater than 0.90. Therefore, Eq. (5.7) can be used to predict the bitumen concentration in oil sand slurries at time \(t\) under the specific operating conditions.
5.2.2 Effect of current density

Effects of the current density on the removal of bitumen versus time are shown in Figure 5.3. The current densities in the experiments varied between 50 and 300 A/m² while the other conditions were kept constant. Figure 5.3 shows that the percentage of bitumen removal (R %) increases with increasing current density up to an optimum value of 150 A/m². Further increase in the current density causes a decrease in the percentage bitumen removal. Initially, increasing the current density enhances the generation of hydrogen and oxygen gases in the flotation cell and therefore, the number of gas bubbles increases; consequently, the attachment of gas bubbles to bitumen is enhanced, thus more bitumen drops are brought up by gas bubbles in the froth layer. When the gas volume increases to a specific threshold at a higher current density (e.g. above 200 A/m²) the bubbles merge with each other, consequently the number of small bubbles reduces, leading to the decrease of bitumen removal rate. Figure 5.4 shows that the first order flotation rate constant (K) increased with increasing current density and decreased after reaching its maximum. The experimental result reveals that there is an optimum current density for removal of bitumen from oil sand tailings slurry. This result indicates that increasing the current density after the optimum level is not feasible for the removal of bitumen. Moreover, higher current density also increases power consumption. Therefore, it was decided that 150 A/m² would be the maximum current density for the removal of bitumen from the MFT slurry.
5.2.3 Effect of pH

The pH in the experiments varied between 3.3 and 10.68 while the other conditions were kept constant. As seen from Figure 5.5, the pH influences the removal of bitumen at different times. A lower removal of bitumen at pH 3.3 was observed as compared to that at pH 8.5, probably due to the effect of bubble sizes. The maximum percentage of bitumen removal (R %) was achieved at pH 6.8 and 8.5. The similar trend was also observed by Ibrahim et al. (2001) in the tests of oil removal. Previous studies (e.g. Khosla et al, 2001) demonstrated that hydrogen bubbles are more effective in separation processes than oxygen bubbles. Raju and Khangaonkar (1984) showed that the sizes of the hydrogen bubbles are larger in an acidic medium than they are in a neutral or alkaline medium. As the minimum hydrogen bubble dimensions occurs in a neutral or slightly alkaline medium, best result achieved at pH 6.8 and 8.5. Smaller bubbles help the flotation process because the smaller bubbles rises at a lower speed, which then have more opportunities for collision with bitumen. As the natural pH of MFT is 8.5, it is decided that pH does not need to be adjusted during EF of bitumen from MFT slurries. Figure 5.6 shows that the first order flotation rate constant (K) increased with increasing pH and decreased after reaching its maximum.

5.2.4 Effect of bitumen concentration

The bitumen concentrations in the experiments were varied between 22.48 mg/L and 314.72 mg/L while the other conditions were kept constant. As seen from Figure 5.7, the bitumen concentration influences the removal of bitumen at different times. Increasing concentrations from 22.48 to 314.72 mg/l enhanced the percentage bitumen removal (R %). For example, the percentage bitumen removals (R %) after 90 min, are 75%, 91.5%
and 94.2% for initial bitumen concentrations 22.5 mg/L, 106.8 and 314.7 mg/l, respectively. The improvement in bitumen removal may be attributed to the fact that a high concentration of bitumen enhances the chance of attachment of gas bubbles on bitumen in the slurry. Qi et al (2013) also demonstrated that during the flotation process, the number of bubbles attached on oil particles is exponentially related to the initial oil concentration. Figure 5.7 also shows that for all initial bitumen concentrations; the percentage removal starts to be stabilized approximately after 30 minutes of flotation. This phenomenon may be due to the different sizes of bitumen drops in the slurry. Once the largest sizes bitumen drops are removed from the flotation cell; the efficiency of the process slows down. Similar trend was observed by Bande et al (2008) for oil field effluent water treatment. Figure 5.8 shows the values of the first order rate coefficient $K$ as a function of the initial bitumen concentration. It reveals that any increase in the bitumen concentration has a positive influence on the reaction kinetics.

5.2.5 Effect of NaCl

In this study, the slurry salinity is changed using NaCl. Most authors (Hosny, 1996, Mansour and Chalbi, 2006, Ibrahim et al. 2001) have used NaCl in electro flotation for separation of oil from oil-water emulsions. NaCl is added in the solution as a supporting electrolyte for adjusting the solution conductivity to achieve desired current density. However, many researchers (Hosny, 1996, Mansour and Chalbi, 2006) demonstrated the additional influence of NaCl on electro flotation for oil removal. Bande et al (2008) observed adding NaCl decreases the size of gas bubbles, especially hydrogen gas, which positively affect the flotation process. In addition Hosny (1996) demonstrated that up to 3.5 % NaCl in the solution doesn’t have any effect on the mechanism of electro-flotation.
Moreover, addition of NaCl reduces the power consumption and hence decreases the operational cost of electro flotation.

To assess the effect of NaCl on removal of bitumen from MFT slurry, a series of batch flotation tests were performed (Experiment no. 3, 13 and 14). Current density, pH and initial bitumen concentration were kept constant throughout the series while the amount of NaCl was varied. Figure 5.9 shows the bitumen removal curves, plotted as a function of time for different dosages of NaCl (17.5 g/kg, 35 g/kg and 70 g/kg). It is found that the addition of NaCl didn’t significantly enhance the bitumen removal. Figure 5.10 shows the values of the first order flotation rate constant (K) as a function of the NaCl dosage. It shows that the increase in NaCl dosage has a slightly positive influence on the flotation kinetics.

Figure 5.11 shows that the electrical power consumption with increasing current density. The current density is the most important parameter for the performance of EF flotation, as described in section 5.2.6 and section 5.2.7. Since the energy consumption is a product of applied current and voltage; in all tests, the applied voltage was reduced and the current density was kept constant in order to minimize power consumption. Figure 5.12 shows the effect of NaCl in decreasing electrical power consumption. For example, at 150 A/m² after 90 minutes of flotation, the electrical power consumptions are 10.5 KWh/m³ and 6.1 KWh/m³ for NaCl dosage of 17.5 g/kg and 70 g/kg, respectively. This is a 41.9 % reduction of power consumption by the increase of NaCl dosage. As evidenced, adjustment of slurry conductivity by adding NaCl can reduce the power consumption significantly.
5.2.6 Key operational parameters for bitumen removal from MFT slurries

The main objective of the study is to reduce the bitumen concentration to below the EPEA maximum discharge limit (10 mg/L). Allen (2008) stated that the bitumen concentrations (as oil and grease) in tailings ponds water have been at least 25 to 90 mg/L and therefore up to 90% removal is required. The final concentration of bitumen in tailings slurry after 90 minutes of flotation has been presented in Figure 5.13, which shows that Exp. nos. 3, 7, 9, 10, 13, 14, 17 and 18 have produced effluent with bitumen concentration less than 10 mg/L. Based on the common characteristics of those experiments, it is clear that the most important operating parameter for bitumen removal by EF is the current density. A current density of 150 A/m² can reduce oil concentration to less than 10 mg/L from a wide range of initial bitumen concentration (22.5 to 106.8 mg/L).

5.2.7 Statistical analysis

5.2.7.1 ANOVA

The objective of the statistical analysis is to decide the most important influencing factors (i.e. current density, pH and initial bitumen concentration) on the performance of removal of bitumen from MFT slurries and their relative significance. This goal is achieved by the analysis of variance (ANOVA), for analyzing data from the two levels three factors full factorial designs (2²) matrix (Exp. no. 1, 3, 6, 9, 15, 16, 17 and 18). In the present study, the experimental data was processed for ANOVA by statistical software MINITAB 15. A confidence level of 95% is used to examine the significance of the studied variables (current density, pH and initial bitumen concentration), hence the P-value less than 0.05 indicates that the effect of corresponding variable is significant on the response of the first
order flotation rate constant (K). The variance ratio denoted by “F” in Table 5.4, is the ratio of the mean square due to a specific influencing factor (e.g. current density, pH and initial bitumen concentration) and the error mean square. In the experimental design, the F ratio is used to determine the relative effect of different variables on flotation rate constant; the larger the F value, the more important that factor is in influencing the response of first order flotation rate constant (K) (Phadke, 1989).

Two levels of current density (50 and 150 A/m²) were selected for statistical analysis as low (-) and high (+) levels, respectively. The ANOVA results in Table 5.4 reveal that the current density is significant on the response of first order flotation rate constant (K) as the P-value is 0.005 (< 0.05). The current density has been found to be the most significant influencing factor on bitumen removal rate constant, because of its lowest P-values. Two levels of pH (3.3 and 8.5) were studied for statistical analysis as low (-) and high (+) levels, respectively. From ANOVA results (Table 5.4), it is clear that the effect of pH is not significant as the corresponding P-value is 0.321 (> 0.05). Two levels of initial bitumen concentration (22.5 and 106.8 mg/L) were selected for statistical analysis as low (-) and high (+) levels, respectively. From ANOVA results (Table 5.4), it is clear that the effect of initial bitumen concentration is significant on first order flotation rate constant (K) as the P-value is less than 0.05. The P-values in ANOVA tables show the order of significant factors as current density > initial bitumen concentration>> pH for bitumen removal from MFT slurries.
5.2.7.2 The Pareto chart

The Pareto chart is used to assess the main and interaction effects of current density, pH and initial bitumen concentration on removal of bitumen from MFT slurries (Figure 5.14). The effects of those factors can be revealed from the horizontal columns in the Pareto chart (Ponnusami et al 2007) with respect to a reference line. As shown in Figure 5.15, the effects of current density and initial bitumen concentration extend beyond the reference line and therefore are potentially important on removal of bitumen from MFT. On the other hand, pH and all other interaction effects are insignificant since they are below the reference line (Mathialagan and Viraraghavan, 2005). The significant effect of current density (A) indicates that 150 A/m² is adequate for maximum removal of bitumen from MFT slurries.

5.3 Summary

An experimental study was carried out to assess the suitability of electro-flotation for removal of bitumen (oil and grease) from oil sand tailings slurry. The following is a summary of the study:

- The effects of operating conditions, such as the current density, pH, bitumen concentration and electrical conductivity adjustment by NaCl on removal of bitumen have been studied. This study shows that all of these parameters have effects on the flotation kinetics and removal of bitumen concentration. Among them, the most important parameter is identified as the current density.
- This study demonstrates that electro-flotation is technically feasible for bitumen removal from oil sand tailings slurry. Based on the data presented in this study; the
maximum removal of bitumen was achieved when the operational parameters were set to the current density of 150 A/m².

- The dosage of NaCl in MFT slurries serves a significant role on reducing the power consumption of EF treatment.
- The kinetics of the electro flotation process for bitumen removal from MFT is best described as a first order reaction.
- The results of statistical analysis, ANOVA, have shown the order of significant factors in the EF process as Current density > initial bitumen concentration>> pH for bitumen removal from MFT slurries.

In conclusion, the results of this research reveal that Electro flotation can be applied for bitumen removal from oil sand tailings slurry.

5.4 References


Alam, R., Shang, J.Q. and Islam, S. 2014. Electrok inetic sedimentation of mature oil sand mine tailings GeoRegina 2014, the 67th Canadian Geotechnical Conference. Regina, Saskatchewan, Canada


Guo 2012. Electrokinetic dewatering of oil sands tailings. MESc. Thesis, Civil and Environmental Engineering, University of Western Ontario


Il’in, V. I., Kolesnikov, V. A., Parshina, Y. I. 2002. Purification of highly concentrated industrial sewage from the porcelain and faience industry by the electric flotation method. Glass Ceram. 59(7-8), 242–244.


### Table 5.1 Properties of Mature Fine Tailings

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Moisture Content (%)</td>
<td>158.40</td>
<td>171.29</td>
</tr>
<tr>
<td>Specific Gravity, Gs</td>
<td>2.58</td>
<td>2.51</td>
</tr>
<tr>
<td>Plastic Limit, PL (%)</td>
<td>36.04</td>
<td>37.43</td>
</tr>
<tr>
<td>Liquid Limit, LL (%)</td>
<td>54.42</td>
<td>51.59</td>
</tr>
<tr>
<td>Plasticity Index, PI (%)</td>
<td>18.38</td>
<td>14.16</td>
</tr>
<tr>
<td>Organic matter (%)</td>
<td>17.92</td>
<td>14.65</td>
</tr>
<tr>
<td>Carbonate content (%)</td>
<td>Not significant (very low)</td>
<td>&lt;1</td>
</tr>
<tr>
<td>D(0.1)um</td>
<td>1.092</td>
<td>0.852</td>
</tr>
<tr>
<td>D(0.5)um</td>
<td>8.034</td>
<td>7.154</td>
</tr>
<tr>
<td>D(0.9)um</td>
<td>26.857</td>
<td>27.911</td>
</tr>
<tr>
<td>Sands (%)</td>
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<td>0.00</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>81.00</td>
<td>80.00</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>19.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Dry Density(g/cm³)</td>
<td>0.49</td>
<td>0.47</td>
</tr>
<tr>
<td>Void Ratio</td>
<td>4.26</td>
<td>4.39</td>
</tr>
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<td>Experiment No.</td>
<td>Current Density (A/m²)</td>
<td>pH</td>
</tr>
<tr>
<td>---------------</td>
<td>------------------------</td>
<td>----</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>8.5</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>8.5</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>8.5</td>
</tr>
<tr>
<td>4</td>
<td>200</td>
<td>8.5</td>
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<td>50</td>
<td>8.5</td>
</tr>
<tr>
<td>18</td>
<td>150</td>
<td>3.3</td>
</tr>
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Table 5.3 Flotation rate constant and Removal of bitumen (%) after 90 min of flotation

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Removal, R (%)</th>
<th>Flotation rate constant</th>
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<tr>
<td></td>
<td></td>
<td>K</td>
</tr>
<tr>
<td>1</td>
<td>71.5</td>
<td>0.015</td>
</tr>
<tr>
<td>2</td>
<td>83.1</td>
<td>0.022</td>
</tr>
<tr>
<td>3</td>
<td>91.6</td>
<td>0.030</td>
</tr>
<tr>
<td>4</td>
<td>78.9</td>
<td>0.019</td>
</tr>
<tr>
<td>5</td>
<td>76.8</td>
<td>0.018</td>
</tr>
<tr>
<td>6</td>
<td>84.2</td>
<td>0.025</td>
</tr>
<tr>
<td>7</td>
<td>92.6</td>
<td>0.031</td>
</tr>
<tr>
<td>8</td>
<td>87.3</td>
<td>0.026</td>
</tr>
<tr>
<td>9</td>
<td>75</td>
<td>0.016</td>
</tr>
<tr>
<td>10</td>
<td>81</td>
<td>0.02</td>
</tr>
<tr>
<td>11</td>
<td>92.8</td>
<td>0.031</td>
</tr>
<tr>
<td>12</td>
<td>94.2</td>
<td>0.033</td>
</tr>
<tr>
<td>13</td>
<td>92.1</td>
<td>0.031</td>
</tr>
<tr>
<td>14</td>
<td>92.6</td>
<td>0.032</td>
</tr>
<tr>
<td>15</td>
<td>50</td>
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<td>16</td>
<td>70.5</td>
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<td>60</td>
<td>0.01</td>
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<tr>
<td>18</td>
<td>75</td>
<td>0.016</td>
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### Table 5.4 Analysis of Variance (ANOVA) for K, using Adjusted SS for Tests

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<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Seq SS</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F</th>
<th>P</th>
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<tr>
<td>Current Density</td>
<td>1</td>
<td>0.0002000</td>
<td>0.0002000</td>
<td>0.0002000</td>
<td>32.00</td>
<td>0.005</td>
</tr>
<tr>
<td>pH</td>
<td>1</td>
<td>0.000008</td>
<td>0.000008</td>
<td>0.000008</td>
<td>1.28</td>
<td>0.321</td>
</tr>
<tr>
<td>Initial Concentration (C0)</td>
<td>1</td>
<td>0.0001445</td>
<td>0.0001445</td>
<td>0.0001445</td>
<td>23.12</td>
<td>0.009</td>
</tr>
<tr>
<td>Error</td>
<td>4</td>
<td>0.000025</td>
<td>0.000025</td>
<td>0.0000063</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>7</td>
<td>0.0003775</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.0025  R-Sq = 93.38%  R-Sq (adj) = 88.41%
Figure 5.1 Schematic of the laboratory scale flotation cell
Figure 5.2 Determination of First Order Rate Constant, $K$ (slope of the straight line)
Figure 5.3 Effect of current density on Removal of bitumen (%)
Figure 5.4 Effect of current density on first order flotation rate constant, $K$ and removal of bitumen (%) after 90 min
Figure 5.5 Effect of pH on Removal of bitumen (%)
Figure 5.6 Effect of pH on first order flotation rate constant, $K$ and removal of bitumen (%) after 90 min
Figure 5.7 Effect of bitumen concentration on Removal of bitumen (%)
Figure 5.8 Effect of bitumen concentration on first order flotation rate constant, K and removal of bitumen (%) after 90 min
Figure 5.9 Effect of NaCl on Removal of bitumen (%)
Figure 5.10 Effect of NaCl on first order flotation rate constant, $K$ and removal of bitumen (%) after 90 min
Figure 5.11 Power consumption rate vs current density (at pH 8.5 and 17.5 g/kg NaCl)

Figure 5.12 Conductivity/ power consumption vs NaCl dosage (g/kg)
Figure 5.13 Concentration of bitumen in final tailings slurry after 90 minutes of flotation
Figure 5.14 Pareto chart of the standardized effects on First Order rate constant.
CHAPTER 6

ELECTROPHORESIS AND ITS APPLICATIONS IN OIL SAND TAILINGS MANAGEMENT1

6 Introduction

Canadian oil sands cover an area of about 142,000 square kilometers (km²) (NEB, 2004). Oil sand tailings, the end products of the oil sands mining operation, are pumped into large tailings ponds. The coarse solids, mostly sands, settle down quickly. However, fine solids, remain suspended in tailings ponds, which take years to consolidate and are known as mature fine tailings (MFT) (Johnson et al., 1993). The MFT is a mixture of residual bitumen, sand, silt, and clay particles. Due to the poor water release ability, low hydraulic conductivity and low strength of the MFT, dewatering under natural conditions is not realistic (Mikula et al., 1996). Currently more than 170 km² of Alberta’s lands are covered by tailings ponds, and expected to occupy an area of 250 km² by 2020, (Government of Alberta, 2012), which causes serious environmental concerns, such as impacts on public health, land use, water supply and air quality (Farkish, 2013). Consequently, various regulations and requirements have been implemented for tailings operations associated with oil sands mining in order to preserve the environment (ERCB, 2009). The main objective in oil sands tailings management is to thicken and consolidate the MFT to reduce

1 A version of this chapter has been presented in GeoRegina 2014, the 67th Canadian Geotechnical Conference, Regina, SK, Canada and subsequently published in the proceedings
the dedicated disposal areas (DDAS) (Farkish, 2013). Several studies have been done on these aspects (Sworska et al, 2000; Guo and Shang, 2014).

The tailings thickening is a dewatering process for slurries with low solid content, in which the first phase is sedimentation of suspended fine solids. Flocculants are commonly used in thickening processes to increase the settling velocity and reduce the thickener size (Jewell and Fourie, 1999). Flocculants are organic, high molecular weight synthetics or natural polymers that help to enhance the settling velocities of suspended solids by adsorbing onto solid particles, forming flocs (Barbour and Wilson, 1993). The centrifuging technique is also an option of thickening, which can produce filter cakes with up to 60 wt. % solids (OSRIN Report, 2010). Filtration is also one of the basic methods by using pressure or a vacuum to separate coarse and medium particles from water (OSRIN Report, 2010).

Electrokinetic thickening is a potential option to enhance the thickening process of fine oil sand tailings. Electrokinetics has been studied extensively in geotechnical engineering applications (e.g. Fourie et al., 2007, Mohamedelhassan, 2008; Rittirong et al., 2008, Shang et al., 2009), including consolidation of soft clays, dewatering of mine tailings, strengthening of marine sediments and so on. The research on dewatering of oil sands MFTs using EK technology has been reported (Guo and Shang, 2014), which focused on the assessment of the effectiveness and efficiency of EK dewatering of MFT.

This study was focused on the electrokinetic sedimentation of the MFT to reduce the settling time. In this study, the MFT is characterized for the composition, followed by a study on the effect of electrokinetic sedimentation (EK). The influencing factors
investigated in this study include the initial solid concentration of the MFT suspension, electric field intensity, electrolytic bubbles, water pH, and the use of an optimized coagulant FeCl$_3$.

6.1 Theory of electrokinetic sedimentation

The thickening of solids in water typically goes through two stages; the first stage is known as sedimentation and the second as consolidation (Mohamedelhassan and Shang, 2001). The sedimentation stage consists of two stages: free settling and hindered settling. At the free settling stage, solids in a suspension are settled at a constant rate. When the free settling stage approaches to an end, a transition stage is observed, which is known as the hindered settling stage. The suspension velocity during the free and hindered settling stages can be expressed as (McRoberts and Nixon, 1976; Russel et al, 1989 and Shang, 1997):

$$U = \beta \cdot u \cdot n'$$  \hspace{1cm} (6.1)

Where $U$ (m/s) is the suspension settling velocity, $u$ (m/s) is the particle settling velocity, $\beta$ is a factor which represents an average velocity of all particles, $n$ is the porosity of the suspension, and $r$ is the coefficient of sedimentation. In the free settling stage, the suspension settling velocity can be computed by replacing porosity, $n = 1$ in Eq. (6.1):

$$U = \beta \cdot u$$  \hspace{1cm} (6.2)

Electrokinetic sedimentation can enhance the free settling velocity significantly of a clay suspension. The principle of electrokinetic sedimentation of clay suspension is discussed by Shang (1997). Clay particles carry permanent negative charges due to the crystal structure and isomorphous substitution when they are in contact with water.
and therefore repel each other when they are suspended in water. Consequently, the suspension remains stable without significant settlement for a long time. When the suspension is subjected to an external dc electric field, the negatively charged particles move towards the positively charged anodes (Shang, 1997). This phenomenon is known as Electrophoresis (EP), which can generate electrokinetic sedimentation. Electrophoresis has been applied to accelerate sedimentation of the Welland River sediment (Buckland et al., 2000) and cohesive soils (Kim et al., 2008).

Mohamedelhassan and Shang (2001) suggested that the overall particle settling velocity subjected to an external dc electric field is the summation of gravity ($u_g$) and electrokinetics ($u_{ek}$):

$$u = u_g + u_{ek}$$  \hspace{1cm} (6.3)

Where, for laminar flow conditions, the classic stock’s laws can be used to represent the settling velocity, $u_g$ of a single, discrete, non-flocculating particle by gravity (Metcalf and Eddy, 1991):

$$u_g = \frac{g(\rho_p - \rho_w)d^2}{18\mu}$$  \hspace{1cm} (6.4)

Where $u_g$ is the particle settling velocity (m/s), $g$ is the gravitational acceleration (m/s$^2$), $\rho_p$ is the mass density of the particles (kg/m$^3$), $\rho_w$ is the mass density of water (kg/m$^3$) and $\mu$ (N-s/m$^2$) is the viscosity of water.
On the other hand, the velocity of individual particles induced by electrophoresis can be expressed as (Shang, 1997; Russel, 1989, Hunter, 1981):

\[
uc_k = \frac{\varepsilon_w \zeta}{\mu} E
\]

(6.5)

Where \(uc_k\) (m/s) is the particles velocity induced by electrokinetics, \(\varepsilon_w\) (F/m) is the permittivity of water, \(\zeta\) (V) is the zeta potential, and \(E\) (V/m) is the electric field intensity.

As the settling velocity of a soil suspension is not uniform due to the wide distribution of grain sizes, therefore, the average particle settling velocity of suspended soil solids can be evaluated as suggested by Mohamedelhassan and Shang (2001):

\[
u = \sum_{i=1}^{N} \left( f_i - f_{i+1} \right) \left( \frac{u_{g(i)} + u_{g(i+1)}}{2} \right) + uc_k
\]

(6.6)

Where, \(f_i\) is the fraction of the suspension finer than the grain size \(d_i\), and \(u_{g(i)}\) is the gravitational settling velocity of an individual particle with the grain size \(d_i\).

Eq. (6.5) suggests that the free settling velocity of particles increases with an increase of the electric field intensity (V/m). However, in reality, if the electric field density exceeds a certain value, the free settling velocity might not increase with electric field intensity. According to the Ohm’s law, the current of a sedimentation column increases with an increase of applied voltage. If the current exceeds a certain value, oxygen bubbles are produced near anode at the bottom of the sedimentation column. According to the Faraday’s law, generating rates of oxygen bubbles from electrolysis of water is directly proportional to the current density (Chen and Chen, 2010). At a high current density, significant amount of O\(_2\) bubbles are generated from the bottom electrode (Anode) as shown in Eq. (6.7)
\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e} \]  

(6.7)

Oxygen bubbles rise to the surface of the sedimentation column and hence negatively affect the overall EK sedimentation process. In an EK sedimentation process, cathode is placed at the top of the slurry; hence the effect of H\(_2\) bubbles generated on the cathode to the sedimentation process is negligible.

Based on above analysis, one can introduce another term in Eq. (6.3), i.e.

\[ u = u_g + u_{ek} - u_f \]  

(6.8)

Where, \( u_f \) is the bubble-particle aggregate velocity acting upward in the EK sedimentation cell. Sarkar (2012) gave an expression for the rise velocity of the bubble-particle aggregate equating the buoyancy, weight and drag forces:

\[ u_f = \frac{g}{18\mu_{pulp} d_b^3} [d_b^3 (\rho_{pulp} - \rho_b) - N_p d_p^3 (\rho_p - \rho_{pulp})] \]  

(6.9)

Where, \( \rho_{pulp} \) is the pulp density, \( \rho_b \) and \( \rho_p \) are the density of bubble and particle respectively, \( \mu_{pulp} \) is the absolute viscosity of pulp; \( d_b \) and \( d_p \) are the dia of bubble and particle respectively. Therefore, the average particle settling velocity of suspended soil solids can be evaluated:

\[ u = \sum_{i=1}^{N} (f_i - f_{i+1}) (f_f) \left( \frac{u_{g(i)} + u_{g(i+1)}}{2} \right) + \frac{\xi \nu \xi}{\mu} E \sum_{i=1}^{N} (f_i - f_{i+1}) (1 - f_f) \left( \frac{u_{f(i)} + u_{f(i+1)}}{2} \right) \]  

(6.10)
Where, \( f_t \) is the fraction of free particle (i.e. not attached to the bubbles). Koh and Schwarz (2006) and Sarkar (2012) gave an expression to estimate the number of particle free at time \( t \) from which \( f_t \) can easily be computed.

\[
f_t = [1 - \int_0^t K_1 N_p N_{bT} dt]^{-1}
\]

(6.11)

Where \( K_1 \) is the particle-bubble attachment rate constant, \( N_p \) is the number of particles and \( N_{bT} \) is the total number of bubbles present in the flotation cell per sec which can be approximated by:

\[
N_{bT} = f_O \frac{Q_O}{\pi d_O^2 / 6}
\]

(6.12)

Where, \( d_O \) is the mean bubble dia of \( O_2 \), \( f_O \) is the fraction of total \( O_2 \) transformed into bubbles. The procedure for determination of \( f_O \) have been described in detail elsewhere (e.g. Vogt, 1984). \( Q_O \) is directly proportional to the current according to the Faraday’s law (Chen and Chen, 2010):

\[
Q_O = \frac{1V_0}{F n_O}
\]

(6.13)

Where, \( Q_O \) (L/sec) is the generating rates of \( O_2 \), at the normal state, \( V_0 \) is the molar volume of gases at the normal state (22.4L/mol); \( F \) is the Faraday’s constant (96,500 C/mol of electrons); \( n_O \) is the electrons transfer number of \( O_2 \) (4 mol electrons per mole of \( O_2 \)). The particle-bubble attachment rate constant, \( K_1 \) can be computed as suggested by Koh and Schwarz, (2006)

\[
K_1 = Z_1 P_a P_s
\]

(6.14)
Where, where \( P_c \), \( P_a \) and \( P_s \) are the probabilities of particle–bubble collision, adhesion and stabilization against external forces and \( Z_1 \) is related to the particle–bubble collision frequency dependent on the size of the particles and bubbles, and hydrodynamics of the flotation pulp. Details procedure for determination of \( Z_1 \), \( P_c \), \( P_a \) and \( P_s \) has been described in detail elsewhere (e.g. Koh and Schwarz, 2006). Eq. (6.10) can be used to predict the average sedimentation velocity induced by a dc electric field by replacing the values into the right-hand side of the equations.

In contrast with the free settling stage, Shang (1997) predicts that the sedimentation velocity of solid suspensions is dominated by the porosity rather than current density in the hindered settling stage. Therefore, it can be assumed that the settlement of a suspension should not be affected significantly by bubbles at hindered settling stage. The experimental agreement with this prediction will be discussed in section 6.4.2.4. Shang (1997) has also given the expressions for electrokinetic sedimentation velocity for the hindered settling stage:

\[
U_{h-ek} = \beta_{h-ek} u_{ek} n_{ek} r_{ek}
\]  

(6.15)

Where \( \beta_{h-ek} \) is the factor that relates the particle’s terminal velocity and suspensions thickening velocity at hindered settling stage and \( r_{ek} \) is the sedimentation coefficient at hindered settling stage.

Substituting, \( u_{ek} \) from Eq. (6.5) in Eq. (6.15):

\[
U_{h-ek} = \beta_{h-ek} \frac{E z e w}{\mu} n_{ek} r_{ek}
\]  

(6.16)
By taking the logarithm of both sides of Eq. (6.16):

$$\ln (u_{h-ek}) = \ln \left( \beta_{h-ek} \frac{E \zeta \varepsilon_w}{\mu} \right) + r_{ek} \ln(n)$$

(6.17)

The electrokinetic sedimentation coefficient $r_{ek}$ represents the slope of the linear relationship between $\ln (u_{h-ek})$ versus $\ln (n)$. Eq. (6.17) has been experimentally verified by several researchers (e.g. Buckland et al. 2000; Islam, 2014) as well as used in the present study as discussed in section 6.3.2.6.

6.2 Materials and Methods

6.2.1 Characterization of Samples

The grain size, liquid limit, plastic limit, plasticity index, specific gravity, dry unit weight, voids ratio, organic matter (%), water pH and zeta potential of MFT recovered from the disposal pond in Fort McMurray, Alberta, Canada were measured. Oil sand mine tailings sample was received in high solid contents. For the measurement of the zeta potential, the tailings sample was diluted at the ratio about 1 to 50 using the same background electrolyte as that in the concentrated suspensions. For doing so, the supernatant was decanted after the particles have settled out and used to dilute the original MFT sample. The diluted tailings sample were titrated from pH 12 to pH 2 by 0.1M NaOH and 0.1M HCL. All measurements were performed using ZetaPlus 2002 analyzer. The particle size was analysed with a laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., UK). X-ray diffraction was carried out using Rigaku-MiniFlex II, powder diffractometer with dry and pulverized samples after passing through #200 sieve (74 microns). The organic content of MFT was determined by the standard ASTM D2974 methods. Solution conductivity and pH were examined following standard methods (APHA, 2005).
6.2.2 Experimental set-up

A testing column (with an inner diameter of 8.8 cm) was used for the EK sedimentation tests. A schematic diagram of the laboratory set up is shown in Figure 6.1. The cathode was made of stainless steel mesh and anode was made of Ti/IrO₂ mesh with the same diameter of the column. The two electrodes were placed in the column, arranged in parallel at 16.5 cm spacing to generate an approximately uniform electric field along the axis of the column.

A slurry of a specific concentration (percent mass/mass) was thoroughly mixed for at least 15 minutes and poured into the sedimentation column. Then a regulated voltage was applied by a dc power supply, directed upward, i.e. the top cathode (-) and bottom anode (+), to induce the downward movement of MFT particles carrying negative charges. The solid–liquid interface of the suspension was measured with real time. The experiments were carried out under various conditions, including different solid concentrations (1 to 5%), electric field intensities (50 to 150 V/m), water pH (8.5 to 12), and the use of an optimized coagulant FeCl₃.

6.2.3 Response Surface Methodology (RSM)

The Response surface methodology (RSM) was employed to find the significance of the two most influencing factors of EK sedimentation, including the initial solid concentration and electric field intensity, based on the response of final solid concentration (%) and free settling velocity (cm/hr) on a 95% confidence interval.
The free settling velocity (cm/hr) was determined by measuring the drop of the solid/solution interface (mud line) as a function of time. A plot of the thickness of the supernatant layer versus time was used to determine the free settling velocity from the slope of the initial linear portion of the plot (Sworska et al, 2000). To define the range of experimental, preliminary experiments were carried prior to the experimental design. A full three-level factorial design was carried out, as shown in Table 6.1. The response variable is expressed as a function of the independent process variables according to the following response surface quadratic model (Montgomery, 2001)

\[
y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2
\]  \hspace{1cm} (6.18)

Where \(y\) is the dependent variable (e.g. free settling velocity (cm/hr) or the final solid concentration(%)\), and \(x_1\) and \(x_2\) are independent variables that represent the initial solid concentration and electric field intensity, respectively; \(\beta_0, \beta_1, \beta_2, \beta_{12}, \beta_{11}\) and \(\beta_{22}\), are the regression coefficients of the model.

The regression analysis for the quadratic equation model was carried out using the Minitab-15 software. Analysis of variance (ANOVA) has been adopted to examine the accessibility of the model. Then, F-test and P-values (probability) with 95% confidence level were used to check for the statistical significance of the quadratic equation model and test variables.
6.3 Results and Discussions

6.3.1 Characterization of tailings

The characteristics of Mature Fine Tailings (MFT) are presented in Table 6.2. The tailings can be characterized as MH according to the Unified Soil Classification system (ASTM D2487), with 81% silt-sized grains, and 19% clay sized grains. The tailings have the liquid limit of 54.42%, plastic limit of 36.04% and plasticity index of 18.38. The specific gravity is 2.58. The moisture content of the tailings as received was 158.4 %, corresponding to the dry density and void ratio of the sample 0.49 g/cm$^3$ and 4.26, respectively. The Organic matter of the sample was 14.65 %. The water pH was 8.5 and corresponding zeta potential was -33mV. The high zeta potential indicates that the tailings suspension is stable. On the other hand, it suggests that the tailings would respond favorably to electrokinetic treatment.

6.3.2 EK sedimentation

6.3.2.1 Effect of electric field intensity

To assess the effect of electric field intensity on EK sedimentation of MFT, a series of batch tests were performed. Figures 6.2, 6.3, and 6.4 show the interface height of MFT slurries versus time under the electric field intensities of 50, 100 and 150 V/m; and initial solid concentrations 1, 3 and 5 %, respectively. The data indicate that with the lower initial solid concentration (1%), the free settling velocity is virtually independent of the electric field intensity (Figure 6.2). On the other hand, with the higher initial solid concentrations (3% and 5%) the settling velocity (cm/h) increases with the electric field intensity (Figure 6.3 and 6.4).
A typical settling curve (interface height vs time) includes an initial stage of stability (due to initial stage of flocculation) followed by a period of relatively rapid settling, and finally a long period of slow settling at a decreasing rate (Kynch, 1952). Different stages of settling curve are shown in Figure 6.3. Figures 6.3 and 6.4 show that for the initial solid concentrations 3% and 5%, the settling velocities under different electric field intensities were almost the same for the first few minutes, then the higher electrical field intensity induced higher settling velocity. The observation indicates that electrophoresis becomes effective from the free settling stage. Similar trend was observed by Kim et al (2008) for Electrokinetic settling of cohesive soils.

The overall effect of the applied electric field intensity on the electrokinetic sedimentation process is illustrated in Figure 6.5. This plot shows the relationship between the final solid concentrations (%) versus the applied electric field intensity (V/m). It is clearly shown that the application of higher external electric field generated sediment of higher solid concentration. The final solid concentration increases linearly with the increasing electric field intensity, as shown in Figure 6.5. Buckland et al. (2000) reported similar trends on the Welland River sediment. Among all electric field intensities studied, 150 V/m produces the highest settling velocity (13.5 cm/hr) (Figure 6.10), as well the highest final sediment concentration (25%) (Figure 6.5).
6.3.2.2 Effect of initial solid concentration

The initial solid concentrations in the experiments varied between 1% and 5%. Figure 6.6 shows the interface height, versus time from gravitational sedimentation tests. It is found that a suspension with the initial solid concentration higher than 5% did not settle at all in 6 hours. The experiment conducted at the suspension of 3% solid concentration also shows that most of the MFT particles are suspended for about 240 minutes, and thereafter very small amount of sedimentation was observed. However, immediate settling of MFT particles was observed on the suspension of 1% solid concentration.

Figures 6.7, 6.8 and 6.9 show the change of the interface height of MFT versus time on suspension of solid concentrations 1, 3, and 5%, under the Electric Field Intensities 50, 100 and 150 V/m, respectively. It reveals that the free settling velocity (cm/h) increased with decreasing solid concentration. This is attributed to the fact that the higher the initial solids concentration, the more hard it is to pass water through the pore spaces in the settling medium. It is also found that the suspension with higher initial solid concentrations (e.g. 5%) stays longer in the initial stability stage, as shown in Figure 6.7, 6.8 and 6.9.

Figure 6.10 shows the relationship between the free settling velocity (cm/hr) and initial solid concentration of suspensions under different electric field intensities. As shown, the relationship is not linear. The figure shows a more accented variation with the concentration until about 3% solids, and then the settling velocity tended to stabilize.

The results indicate that the initial solid concentration of the MFT plays an important role in the electrokinetic sedimentation process. The optimal effect of electrokinetic sedimentation was achieved in the solid concentration of 5% mass/mass, in which
significant enhancement was achieved in terms of the increase in the final solid concentration (25 %). The experiments was repeated three times for 5% solid content to investigate the reproducibility of the experiments. The results of the 3 experiments are very consistent. The free settling velocity of the suspension for 5% solid content under 150 V/m was 4.8 ± 0.15 cm/hr. It is also noted that though the suspension with 3% solid content induces faster settling velocity compared to that of 5% solid content, the final interface height were almost the same under electric field intensity of 150 V/m (Figure 6.9). Therefore, an electric field intensity of 150V/m along with an initial solid concentration of 5% can be used as an optimum operating condition for EK sedimentation of MFT.

6.3.2.3 Effect of pH

The effects of pH on the interface height versus time are shown in Figure 6.11. As shown, the suspension with water pH 10 has significantly higher settling velocity (12 cm/hr) compared to that of pH 8.5 (4.8 cm/hr). This is attributed to the effect of pH to the zeta potential, as shown in Figure 6.12. If an alkali (e.g. NaOH) is added in the tailings slurry the zeta potential of clay become more negative, which facilitate EK sedimentation. However, pH should not be increased further as it might increase the conductivity of the slurry. As a result current density in the sedimentation cell might increase which will negatively affect the overall sedimentation process due to the generation of O₂ bubbles as described by Alam et al (2014). The effect of bubbles on EK sedimentation of MFT has been described in the following section 6.3.2.4.
6.3.2.4 Effect of bubbles on EK sedimentation

Though Eq. (6.6) suggests that the free settling velocity of particles increases with an increase of the electric field intensity (V/m); however in reality, increasing the electric field intensity after the optimum level does not increase the free settling velocity because of formation of bubbles, as discussed in section 6.1. Islam (2014) studied experiments on EK sedimentation of oil sand tailings slurry at higher electric field intensity (up to 281.25 V/m). It was reported that the corresponding current density was about 25 A/m². Figure (6.13) shows that further increase of current density above 20 A/m² does not improve the free settling velocity of oil sand tailings slurry significantly due to the negative effect of bubbles in the sedimentation column.

The electric field intensity is not the only parameter leading to the increase in the current density in the sedimentation column. A higher electrical conductivity can also increase the current density. To assess the effect of electrical conductivity on EK sedimentation of MFT, a series of batch tests were performed under the same electric field intensity (150 V/m). The current density was increased by adding KNO₃ salt to the slurry samples. Figure 6.14 shows the interface height of MFT slurries versus time under the initial current densities of 7 A/m² (no salt was added), 45 A/m² (by adding 0.035 M KNO₃) and 70 A/m² (by adding 0.06 M KNO₃) under a constant electric field intensity (150 V/m). It reveals that the free settling velocity decreased with higher current density. This is attributed to the fact that the bubbles generated at the bottom electrode significantly reduce the free settling velocity at higher current density. The findings of the study show that bubble effect should be considered (as described in Eq. 6.10) to predict the settling velocity of MFT slurry in the free settling stage. The results also suggest that the current density of EK sedimentation
of MFT should not be increased to more than 20 A/m² to control the bubble effect and reduce power consumption in the free settling stage.

On the other hand, the negative effect of high current density on the hindered settling stage was found to be insignificant. This is attributed to the fact that the high current densities (over 45 A/m²) do not sustain during the hindered settling stage, as observed in the experiments. Figure 6.15 shows that the initial current density was up to 70 A/m² (by adding salt) at the beginning of the experiment, whereas it dropped to 12 A/m² in the hindered settling stage. In the hindered settling stage the porosity of the slurry reduced significantly compared to that at free settling stage. As a result the electrical resistivity of the slurry increased significantly, leading to the decrease in the current density.

6.3.2.5 Comparison with coagulation

The comparisons for the effects of coagulation and EK on settlement of MFT are shown in Figure 6.16. A 350 mg/L FeCl₃ solution (optimized dosage from jar tests) was added to the slurry with the initial solid content of 5%, which generated sedimentation of the slurry samples. At the end of the test, the final interface height of the sediment was 10.3 cm after 6 hours of adding FeCl₃ (Figure 6.16). On the other hand, in the test on the slurry of 5% solid content the final interface height was about 3.5 cm for EK sedimentation after 6 hours. In conclusion, The EK sedimentation is shown to be more effective than coagulation.
6.3.2.6 Coefficients of EK sedimentation

The coefficients, $r_{ek}$ (Eq. 6.17) of EK sedimentation is an important indicator of the overall performance in the hindered settling stage. Lower values of $r_{ek}$ represent quick settlement of the tailings slurry. The coefficients, $r_{ek}$ of MFT have been calculated from Eq. 6.17 as suggested by Shang (1997). According to Eq. 6.17, ln ($u_{h-ek}$) and ln ($n$), yield a linear relationship if $r_{ek}$ is constant. The values of $r_{ek}$ and corresponding $R^2$ values obtained from all experimental data based on the linear relationship between ln ($u_{h-ek}$) and ln ($n$), for 5\% solid content are summarized in Table 6.3. The value of sedimentation coefficient, $r_{ek}$, for 5\% solid content at 150 V/m is 31.10, which is consistent with the result that found by Islam (2014). The values of $r_{ek}$, decrease with an increase in the applied electric field intensity, as seen in Table 6.3. Buckland et al. (2000) also found the similar trend for the EK sedimentation of Welland River sediment. Based on the previous results as well as the results obtained from this study, it can be concluded that Eq. (6.17) is valid for modeling of clay suspensions in the hindered settling stage.

6.3.2.7 Development of regression model

The two responses (final Solid Concentration (%) and free settling velocity, cm/hr) were correlated with two most important factors of the EK sedimentation process, i.e. the initial solid concentration and electric field intensity, using the second order polynomial, Eq. From the experimental data (Experimental conditions are shown in Table 6.1 and experimental results are plotted in Figures 6.5 and 6.10), the following quadratic regression models were established for the final Solid concentration (%) and settling velocity, (cm/hr),
Final Solid Concentration (%) = 10.4271 - 1.923x1 + 0.088x2 + 0.251x1^2 + 0.000495x2^2 + 0.0257x1x2

\[(R-Sq = 98.24\% \text{ R-Sq (adj) } = 95.32\%)

Free Settling velocity (cm/hr) = 18.790 - 7.455x1 + 0.0108x2 + 0.767x1^2 + 0.00011x2^2 + 0.00495x1x2

\[(R-Sq = 99.07\% \text{ R-Sq (adj) } = 97.53\%)

The R-Sq (adj) values are 95.32% and 97.53% for the final solid concentration (%) and free settling velocity (cm/hr), respectively. The data fit well in the regression model. The model was assessed using Fisher’s statistical test (F-test) for ANOVA. Tables 6.4 and 6.5 show the ANOVA results for the final solid concentration and free settling velocity, respectively. The P-value is used to judge whether the F-statistics is large enough to indicate statistical significance. A P-value lowers than 0.05 indicates that the model is considered to be statistically significant (Jaikumar and Ramamurthi, 2009). Tables 6.4 and 6.5 demonstrate the quadratic regression models of the final solid concentration (%) and free settling velocity (cm/hr) are statistically significant at the 95% confidence level since the P-values are less than 0.05.

6.3.2.8 Relative significance of initial solid concentration and electric field intensity

It was found that both initial solid concentration and electric field intensity have a strong effect on the EK sedimentation of the MFT. The significance of those two variables was analyzed using the t test. In general, the larger the magnitude of the t-value and smaller the P value, the greater is the significance of the corresponding coefficient term. From the
Student’s t-test results it was observed that both the initial solid concentration and electric field intensity are equally significant on the response of final solid concentration (%) as the P-value is 0.003 (< 0.05) (Table 6.6). Their interaction effect is also found to be significant as the corresponding P-value is 0.025 (< 0.05) (Table 6.6).

The t-test results in Table 6.7 reveal that both the initial solid concentration and electric field intensity are significant on the response of free settling velocity, as the P-values are less than 0.05. However, the coefficients in the quadratic term for the initial solid concentration (P-value = 0.001) are more significant compared to coefficients in the quadratic term for the electric field intensity (P-value = 0.020 >0.001).

Figures 6.17 and 6.18 show the contour plots based on the model to present the influence of the initial solid concentration (%) and electric field intensity on final solid concentration (%) and free settling velocity (cm/hr) respectively. Figure 6.17 shows that the final solid concentration increases with increasing either initial solid concentration or electric field intensity. However, the highest final solid concentration (> 24 %) was obtained with high initial solid concentration and high electric field intensity. The shape of the contour map for the settling velocity strongly depends on the solid concentration, as depicted in Figure 6.18. The highest settling velocity (> 12 cm/hr) was obtained in the low initial solid concentration range.
6.4 Summary

The effects of operating conditions of EK sedimentation are investigated, including the initial solid concentration of the tailings suspension, electric field intensity, pH, electrolytic bubbles and the use of an optimized coagulant FeCl$_3$ on settlement of MFT. The results indicate that all of these parameters have effects on the EK sedimentation process. It is found that the application of an external electric field significantly shortened the sedimentation time. Moreover, the performance of EK is better than coagulation. The slurry pH has a significant effect on EK sedimentation due to its effect on zeta potential of MFT. Electrolytic bubbles negatively affect the EK sedimentation process, especially at the high current density. A numerical equation has been proposed to predict the average settling velocity in the free settling stage.

From the Student’s t-test results, it is concluded that both initial solid concentration and electric field intensity are equally significant on the final solid concentration in the EK sedimentation. The effect of initial solid concentration is more significant compared to the electric field intensity on the response of free settling velocity.

6.5 References


**Table 6.1** Factors and levels used in the full three-level factorial design

<table>
<thead>
<tr>
<th>Variable</th>
<th>Low (-1)</th>
<th>Medium (0)</th>
<th>High (+1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid Content (%)</td>
<td>1</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Electric field intensity (V/m)</td>
<td>50</td>
<td>100</td>
<td>150</td>
</tr>
</tbody>
</table>
Table 6.2 Characteristics of MFT

<table>
<thead>
<tr>
<th>Name of sample</th>
<th>MFT (Oil Sands Tailings)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Moisture Content (%)</td>
<td>158.4</td>
</tr>
<tr>
<td>Specific Gravity, Gs</td>
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</tr>
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<td>Atterberg Limits</td>
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</tr>
<tr>
<td>Plastic Limit, PL (%)</td>
<td>36.04</td>
</tr>
<tr>
<td>Liquid Limit, LL (%)</td>
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<tr>
<td>Plasticity Index, PI (%)</td>
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</tr>
<tr>
<td>Organic matter (%)</td>
<td>14.65</td>
</tr>
<tr>
<td>Carbonate content (%)</td>
<td>Not significant</td>
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</tr>
<tr>
<td>D(0.1) µm</td>
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</tr>
<tr>
<td>D(0.5) µm</td>
<td>8.034</td>
</tr>
<tr>
<td>D(0.9) µm</td>
<td>26.857</td>
</tr>
<tr>
<td>Sands (%)</td>
<td>0.00</td>
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<tr>
<td>Silt (%)</td>
<td>81.00</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>19.00</td>
</tr>
<tr>
<td>Dry Density (g/cm³)</td>
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</tr>
<tr>
<td>Void Ratio</td>
<td>4.26</td>
</tr>
<tr>
<td>pH</td>
<td>8.5</td>
</tr>
<tr>
<td>Zeta Potential(at natural condition)</td>
<td>-33mV</td>
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Table 6.3 Values of $r_{ek}$ and corresponding $R^2$

<table>
<thead>
<tr>
<th>Solid Content</th>
<th>Electric Field Intensity</th>
<th>$r_{ek}$</th>
<th>$R^2$</th>
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</thead>
<tbody>
<tr>
<td>5</td>
<td>50</td>
<td>245.19</td>
<td>0.9115</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>91.15</td>
<td>0.905</td>
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<td>5</td>
<td>150</td>
<td>31.10</td>
<td>0.93</td>
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Table 6.4 Analysis of Variance (ANOVA) for Final Solid Concentration (%)

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<thead>
<tr>
<th>Source of variation</th>
<th>Sum of squares</th>
<th>Mean square</th>
<th>F-value</th>
<th>P-value</th>
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</thead>
<tbody>
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<td>Regression</td>
<td>257.63</td>
<td>51.52</td>
<td>33.5</td>
<td>0.008</td>
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<tr>
<td>Residual Error</td>
<td>4.607</td>
<td>1.536</td>
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<tr>
<td>Residual Error</td>
<td>262.23</td>
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Table 6.5 Analysis of Variance (ANOVA) for settling velocity (cm/hr)

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Sum of squares</th>
<th>Mean square</th>
<th>F-value</th>
<th>P-value</th>
</tr>
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<tr>
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<td>32.7091</td>
<td>64.06</td>
<td>0.003</td>
</tr>
<tr>
<td>Residual Error</td>
<td>1.532</td>
<td>0.5106</td>
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<tr>
<td>Residual Error</td>
<td>165.078</td>
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Table 6.6 Regression coefficient of full polynomial model for Final Solid Concentration (%) (in coded units)

<table>
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<tr>
<th>Coefficient</th>
<th>Parameter estimate</th>
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<th>P</th>
</tr>
</thead>
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<tr>
<td>$\beta_0$</td>
<td>10.714</td>
<td>11.599</td>
<td>0.001</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>4.307</td>
<td>8.513</td>
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<tr>
<td>$\beta_2$</td>
<td>4.375</td>
<td>8.647</td>
<td>0.003</td>
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<td>$\beta_{11}$</td>
<td>1.005</td>
<td>1.146</td>
<td>0.335</td>
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<tr>
<td>$\beta_{22}$</td>
<td>1.238</td>
<td>1.413</td>
<td>0.253</td>
</tr>
<tr>
<td>$\beta_{12}$</td>
<td>2.570</td>
<td>4.148</td>
<td>0.025</td>
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Table 6.7 Regression coefficient of full polynomial model for settling velocity (cm/hr) (in coded units)

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Parameter estimate</th>
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<tbody>
<tr>
<td>$\beta_0$</td>
<td>4.8533</td>
<td>9.112</td>
<td>0.003</td>
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<td>$\beta_1$</td>
<td>-4.7100</td>
<td>-16.145</td>
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<td>$\beta_2$</td>
<td>1.3200</td>
<td>4.525</td>
<td>0.020</td>
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<td>$\beta_{11}$</td>
<td>3.0700</td>
<td>6.076</td>
<td>0.009</td>
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<tr>
<td>$\beta_{22}$</td>
<td>0.2800</td>
<td>0.554</td>
<td>0.618</td>
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<td>$\beta_{12}$</td>
<td>0.4950</td>
<td>1.385</td>
<td>0.260</td>
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Figure 6.1 Schematic diagram of the laboratory set up
Figure 6.2 Effect of electric field intensity under 1% solid concentration on surface settlement vs time of MFT
Figure 6.3 Effect of electric field intensity under 3% solid concentration on surface settlement vs time of MFT
Figure 6.4 Effect of electric field intensity under 5% solid concentration on surface settlement vs time of MFT.
Figure 6.5 Effect of Electric field intensity on Final Solid Concentration (%)
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CHAPTER 7

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

This research is on the study of fundamentals and potential applications of electro-flotation and electrokinetic sedimentation in oil sand tailings management. The results from experiments and analytical models indicate that the electro-flotation and electrokinetic sedimentation can serve as viable tools for bitumen removal and sedimentation of fine oil sand tailings.

7.1 Summary

The study includes four main schemes: (1) Electrochemical model development to interpret the electrolysis voltage required in an electro-flotation (EF) process; (2) Investigation of the bubble size distribution of hydrogen and oxygen produced from Stainless steel (SS 316) and Ti-IrO₂ (DSA) electrodes; (3) Laboratory scale study to investigate the performance EF for removal of bitumen from oil sand tailings slurry; and (4) Laboratory scale study to assess the performance of electrokinetic (EK) sedimentation for thickening of mature fine tailings (MFT), with focus on reducing the settling time and increasing the solid content.

An electrochemical model is presented to represent the relationship between the total cell voltage and variables, such as the equilibrium potential difference for water split, anode activation overpotential, anode concentration overpotential, cathode activation overpotential, cathode concentration overpotential and ohmic overpotential in an electro
flotation process, based on the Nernst equation, Tafel equation, Fick’s model, and Ohm’s law. The simulation results are compared with experimental data from this study as well as with data obtained from the literature.

The bubble size is measured in a lab scale EF cell using a high-speed camera. The influence of current density, water pH and ionic strength, electrode materials, and frother concentration on both hydrogen and oxygen bubble sizes is investigated. Furthermore, four mathematical distributions (normal, log-normal, Weibull (Rosin–Rammler) and gamma distributions) are fitted to the experimental data to assess the mathematic distributions of bubble sizes in an EF cell.

The separation of bitumen from mature oil sand tailings slurries by electro-flotation is carried out in an EF cell equipped with Ti-IrO₂ mesh as anode and stainless steel (SS 316) mesh as cathode. The effects of operating parameters, such as water pH, current density, bitumen concentration, and NaCl dosage on the performance of batch cell flotation are examined. An analysis of Variance (ANOVA) is carried out to assess the statistical significance of influencing factors with respect to the first order flotation rate.

The suitability of EK sedimentation to accelerate thickening of MFT is investigated. A series of laboratory-scale column experiments are carried to examine the effects of electrophoresis during settling processes. The investigation focuses on the effects of EK sedimentation as related to the initial solid concentration of the tailings suspension, electric field intensity, electrolytic bubbles, water pH, and the use of an optimized coagulant FeCl₃. A numerical equation has been proposed to predict the average settling velocity in the free settling stage.
7.2 Conclusions

I. The conclusions from the study of electrochemical model of electro-flotation are as follows:

- The bubble fractions between the anode and cathode are 30% to 35%, respectively. The bubbles significantly increase the electrical resistance and the overall electrical potential of an EF cell.

- Among all approaches used to measure the cell resistance in this study, the Bruggeman Eq. is the best fit for EF.

- The results of simulation based on the proposed electro-chemical model representative of the relationship between the total cell voltage and other variables are compared with experimental data of this study as well as with data obtained from the literature, and good agreement is found. The models can be used to calculate the required electrolysis voltage for an EF cell under different operating conditions.

II. The following conclusions are reached based on the bubble size distribution in the laboratory scale electro- flotation study:

- The experimental data obtained from the tests conducted in the lab scale EF cells are well represented by the log-normal distribution.

- The water pH has significant effect on bubble sizes. The smaller bubbles of H₂ at the cathode are observed at near neutral pH values, whereas smaller bubbles of O₂ at the anode are observed in low pH water.

- The Current density has significant effect on the bubble size. The mean bubble size decreases with the increase in the current density up to a threshold value of 100
A/m$^2$. Further increase in the current density causes an increase in bubble sizes, which is attributed to the coalescence of free moving bubbles.

- The study on the frother (Tennafroth 250) shows that with increasing frother concentration, the bubble size decreased until a critical coalescence concentration (CCC) is reached. At concentrations above CCC, no further changes in the bubble size are observed.

- A slight decrease in the bubble size is observed with the increase of ionic strength (by adding KNO$_3$).

- It is found that when used as the anode, the Ti/IrO$_2$ plate produces finer O$_2$ bubbles than the stainless steel SS 316 plate.

III. The following conclusions are reached based on experimental data on removal of bitumen from mature oil sands tailings slurries by electro-flotation:

- The operating conditions, such as the current density, pH, bitumen concentration and electrical conductivity adjustment by NaCl, have effects on the flotation kinetics. Among them, the most important operating parameter is identified as the current density.

- Based on the data presented in this study, the maximum bitumen removal is achieved at the current density of 150 A/m$^2$.

- The dosage of NaCl in MFT slurries serves a significant role on reducing power consumption of EF treatment.

- The kinetics of the EF process for bitumen removal from MFT is best described as a first order reaction.
The results of statistical analysis, ANOVA, have shown that for bitumen removal from MFT slurries by an EF process, the order of significant factors is: current density > initial bitumen concentration > pH.

IV. The study on the Electrophoresis and its applications in oil sand tailings management leads to the following conclusions:

- The initial solid concentration of the tailings suspension, electric field intensity, pH and electrolytic bubble affect the EK sedimentation process.
- The application of an external electric field significantly reduces the sedimentation time. The performance of EK is better than chemical coagulation (by using the optimum dosage of FeCl$_3$).
- The pH of the MFT slurry has a significant effect on EK sedimentation due to its impact on the zeta potential.
- Electrolytic bubbles reduce the effectiveness of the EK sedimentation process, especially at a higher current density, attributed to the rise of bubble-particles aggregate to the surface of MFT suspension.
- From the Student’s t-test results, it is concluded that the initial solid concentration and electric field intensity are equally significant on the final solid concentration in the EK sedimentation. On the free settling velocity, on the other hand, the effect of initial solid concentration is more significant than the electric field intensity.
7.3 Recommendations for further study

The results from experiments and analytical models indicate that the electro-flotation and electrokinetic sedimentation are feasible for bitumen removal and thickening of fine oil sand tailings. It is recommended that the following should be studied in future research:

- In this study, the bubble size measurement was restricted to the electrodes of two materials (Stainless steel (SS 316) and Ti-IrO₂ (DSA)) without considering any liquid flow. Further research should be performed to study the effect of flow kinetics on the bubble size using various electrode conditions (geometry, materials etc.). Moreover, a theoretical model should be developed to predict the bubble size at the time of detachment from the electrodes and their subsequent growth.

- The experiment on separation of bitumen from MFT slurries by EF was carried in a laboratory scale flotation cell. A pilot-scale experiment should be designed, tested and monitored on EF of MFT using the optimized operating conditions obtained from laboratory studies. The effect of electrolytic gases on the surface of MFT minerals as well as on residual bitumen should be investigated. The feasibility of separation, collection and storage of hydrogen gas releasing from EF cell should be studied as a source of energy.

- The study on EK sedimentation was carried out in batch tests. A continuous sedimentation system should be developed for large scale thickening. The viscosity of tailings slurry has strong effect on the settling velocity of MFT. Therefore, a
study should be carried out to examine the efficiency of EK sedimentation by reducing the viscosity of slurries at higher temperature. There is a possibility of MFT solids oxidation due to the redox reactions at the anode. Hence the quality of thickened solids should be monitored. Moreover, a cost-benefit analysis of the technology is recommended for the design of in-situ implementation.
APPENDIX A

SERVICE LIFE ANALYSIS OF Ti/IrO₂

Service life of materials is one of the most important factors to select it as anode materials. The electrode service life is strongly dependent on the current density used. For example, Ti/ RuO₂-TiO₂ electrodes could be used for only 18 h at 20 000 A/m² in 2M HClO₄ plus 0.2M NaCl solution, on the other hand, when the current density was lowered to 5000 A/m², the accelerated lifetime increased to about 200 h (Hine et al, 1979). Similar trend was reported by Malkin (1982). They reported 25 times higher accelerated service life at 1600 A/m² than at 16 000 A/m². A simple model relating the service life (SL) to the current density (i) have been obtained (Chen et al, 2001):

\[ SL \propto \frac{1}{i^n} \]  
(A.1)

where \( n \) ranges from 1.4 to 2.0. In the present study, the service life (SL_{EF}) of Ti/IrO₂-Ta₂O₅ for EF application at a current density (i_{EF}) is estimated as suggested by Chen et al, (2001):

\[ SL_{EF} = SL_a (\frac{i_a}{i_{EF}})^n \]  
(A.2)

where \( SL_a \) and \( i_a \) are the service life and the current density under the accelerated life test conditions. In the present study, to investigate the service life of Ti/IrO₂-Ta₂O₅, an electrode cell was formed by Ti/IrO₂-Ta₂O₅ with two brass cathodes. The electrodes dipped into a beaker which have 600ml of 25% H₂SO₄ and the cell temperature was higher than
45°C during the electrodes working with the applied current density 10667 A/m². Figure A-1 displays the potential change during the accelerated life test. The initial potential obtained was 4.37 V which was found almost unchanged for 500 h. No sharp potential increase was observed during the test, indicating no failure of the electrode. No cracks and pores were exposed after the accelerated life test. Therefore, the surface of titanium substrate was covered well with the coating at the end of the accelerated life test. Usually, the current density used in EF is below 300 A/m² (Chen et al, 2002a). Assume an average \( n \) of 1.7 and a current density of 300 A/m², then \( \text{SL}_{\text{EF}} = \text{SL}_a \left( \frac{i_a}{i_{\text{EF}}} \right)^n = 500 \left( \frac{10667}{300} \right)^{1.7} \approx 24 \) years, comparable with that of Ti/IrOₓ-Sb₂O₅-SnO₂ (~20 years) tested by Chen et al (2002b) under same value of \( n \) and current density. However, it is explicable that the true electrode lifetime in real industrial application may be shorter than that estimated here due to the possible mechanical wear of the activated coating film (Chen, 2002b).

References


Figure A-1 potential changes during accelerated life test in 25% H\textsubscript{2}SO\textsubscript{4} solution at 4.8 amps at 45\textdegree{}C.
APPENDIX B

MEASURING BITUMEN CONCENTRATION BY ASTM D7575

B1 Apparatus

A onetime extractor equipped with infrared-amenable oil and grease solid phase extraction membrane was used in this experiment to extract bitumen from tailings slurry. A set of seven devices with a specified amount of oil and grease was used for calibration. A onetime use plastic syringe (10 mL) was used to collect the samples. A drying system capable of drying the extractor sufficiently for infrared analysis was used. Analyses were performed with a FTIR spectrometer (Nicolet 6700) using the wave number of 2920 cm$^{-1}$.

B2 Experimental Procedure

10 mL sample was taken from the flotation unit in a syringe. Then the syringe was attached with the extractor. The samples were passed through the extractor at 5 mL/min. Sample was being processed carefully so that no leaking was occurred. Then the extractor was attached onto the Luer-Lok fitting of the drying manifold in such a way that the extractor remained upright. Then the air was flown through the extractor for dryness. A clean and unused extractor was placed into the sample card in the spectrometer beam and a 200 scan reference was recorded. Then the processed extractor was loaded into the sample card and 50 scan absorbance spectrum was collected. The height of the peak at 2920 cm$^{-1}$ was measured using the baseline endpoints of 2800 cm$^{-1}$ and 2990 cm$^{-1}$. Then the concentration of bitumen (mg/L) was measured by the following equation:
Total bitumen (mg/L) = (AB+C) (10/D)

Where, A is the height of peak at 2920 cm\(^{-1}\), B is the slope of linear calibration, C is the intercept of linear calibration and D is the total volume processed.
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