Emulsification by Penetration of Particles from Water into Diluted Bitumen

by

Jayant Borana

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Department of Chemical Engineering and Applied Chemistry
University of Toronto

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Abstract

In this work, we demonstrate that the fine droplets of water in bitumen could be formed by the penetration of a particle from process water into diluted bitumen under the influence of an impinging force. The sizes of the smallest emulsified droplets produced in the experiments were close to 1.9μm. A careful examination of the penetration process revealed two broad categories of emulsification mechanisms: pinch-off and residual tail emulsification. It was also found that the residual tail emulsification mechanism was induced by surfactant mediated tip-streaming. At higher χ, the disintegration of fine threads resulting from the penetration process lead to the formation of satellite and sub-satellite formation of sizes 2-3 μm. The observations and trends from this work were used to examine the possibility of emulsification via the penetration mechanism on the industrial scale, and potential emulsification locations in the froth treatment section of bitumen production were identified.
First and foremost, I would like to take this opportunity to express my deep and sincere gratitude to my thesis supervisor, Prof. Arun Ramchandran, for his valuable suggestions, discussions and immense support throughout the course of my stay at the University of Toronto. This thesis would not have taken this shape without his tremendous support during the writing process. I am also grateful to Prof. Edgar Acosta and Dr. Samson Ng (Syncrude Canada Ltd.) for their valuable suggestions and recommendations during biannually organized UofT-Syncrude meeting here at University of Toronto. I am also grateful to Prof. Edgar Acosta for providing the droplet size distribution of diluted bitumen froth sample data obtained from acoustic spectrophotometry and granting me permission to use the equipment available in his lab for sample preparation and interfacial tension measurement. I would like to acknowledge Syncrude Canada and NSERC for funding this project. I am thankful to Syncrude Canada for providing bitumen samples to conduct experiments.

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-Jayant Borana
# Table of Contents

Acknowledgments ........................................................................................................................................ iii
Table of Contents ........................................................................................................................................ iv
List of Figures .............................................................................................................................................. vi
List of Abbreviations and Symbols .......................................................................................................... x

Chapter 1 Introduction and Motivation ..................................................................................................... 1
  1.1 Oil sands overview ................................................................................................................................. 1
  1.2 Motivation ............................................................................................................................................. 2

Chapter 2 Literature Review ...................................................................................................................... 6
  2.1 Mechanisms for emulsification of extremely fine water droplets in bitumen ................................. 6
    2.1.1 Spontaneous emulsification ............................................................................................................ 6
    2.1.2 Tip-streaming .................................................................................................................................. 6
    2.1.3 Satellite droplet formation ........................................................................................................... 8
  2.2 Hydrodynamics of particle interaction with a liquid-liquid interface ............................................. 8
    2.2.1 Creeping motion of particles at the interface .................................................................................. 9
    2.2.2 Inertial settling of particles through an interface ........................................................................ 11
    2.2.3 Particle penetration time ............................................................................................................. 12
  2.3 Summary ............................................................................................................................................. 12

Chapter 3 Materials and Methods .......................................................................................................... 15
  3.1 Materials ............................................................................................................................................. 15
  3.2 Device fabrication ................................................................................................................................. 15
  3.3 Hydrophobization for model system experiments ............................................................................. 16
  3.4 Design of experimental operating parameters ................................................................................... 16
    3.4.1 Bitumen dilution ............................................................................................................................ 16
    3.4.2 Solvent .......................................................................................................................................... 17
    3.4.3 Process water composition ......................................................................................................... 17
    3.4.4 Particle size ................................................................................................................................. 17
    3.4.5 Force acting on a particle ............................................................................................................. 17
  3.5 Sample preparation ............................................................................................................................... 18
3.5.1  Particles separation ................................................................. 18
3.5.2  Bitumen solution preparation .................................................. 18
3.5.3  Process water preparation ....................................................... 18
3.5.4  Bitumen saturation with process water ..................................... 19
3.6  Experimental setup ..................................................................... 19
3.7  Forces acting on a particle .......................................................... 21
  3.7.1  Drag coefficient for non-spherical particles ............................. 24
  3.7.2  Drag Coefficient Correction to Incorporate Wall-Effect ........... 24
  3.7.3  Magnetic Force on a Particle .................................................. 25
  3.7.4  Error Analysis ....................................................................... 26
Chapter 4 Results and Discussions .................................................... 28
  4.1  Model system – mineral oil and aqueous-organic solution .......... 28
    4.1.1  Particle Penetration across mineral oil and aqueous-organic sol\textsuperscript{i} interface ....... 28
    4.1.2  Classification of emulsification type .................................... 30
    4.1.3  Effect of viscosity .................................................................. 32
    4.1.4  Effect of interfacial tension ................................................... 34
  4.2  Bitumen system – bitumen solution and process water ............ 34
    4.2.1  Particle penetration across bitumen solution and process water interface ............. 34
    4.2.2  Emulsification outcomes ...................................................... 39
    4.2.3  Residual tail diameter .......................................................... 41
    4.2.4  Water droplets size distribution .......................................... 43
    4.2.5  Effect of bitumen dilution and process water pH ................... 47
    4.2.6  Effect of particle size .......................................................... 48
    4.2.7  Particle penetration time ...................................................... 49
    4.2.8  Total emulsified water volume ............................................ 50
    4.2.9  Particle Interaction with the bitumen-water interface in the extraction and froth treatment process: ........................................ 51
Chapter 5 Conclusions and Future Work ................................................. 56
  5.1  Conclusions ............................................................................... 56
  5.2  Future work ............................................................................... 58
References ............................................................................................. 60
List of Figures

Figure 1. Schematic of synthetic crude oil (bitumen) production from oil sands using Clark hot-water extraction, froth floatation, froth treatment, and upgrading process. (adapted from Masliyah et al. [3]) ................................................................. 2

Figure 2. Acoustic resonance spectrometer shows a bimodal distribution of sub-micrometer and micrometer size water droplets in bitumen froth, diluted under mild mixing conditions. ............. 3

Figure 3. Boundary integral simulation of a particle with a constant force penetrating through water-oil interface: (A) a particle (black dot) pushed against a drop by a force $F$, (B) a zoomed-in view of the penetration of the particle from water into oil. ........................................... 4

Figure 4. A schematic of tip-streaming process. Adsorption and desorption of the surfactants at the interface. Elongational flow past the droplet stretches the interface and sweeps the surfactants to generate concentration gradient, it leads to form a tip with ultralow interfacial tension. A thread is released from the tip which breaks up to form droplets. (adapted from Anna et al. [21]) .......... 7

Figure 5. Schematic diagram of a particle interaction at an interface. .......................................................... 9

Figure 6. Schematic diagram of creeping motion of a particle near a deformable Fluid A and Fluid B interface. .................................................................................................................. 10

Figure 7. Inertial settling of a sphere through a deformable interface, and emulsification via end-pinching.............................................................................................................. 11

Figure 8. Schematic of glass microdevice fabrication, (A) aligning glass slides with spacers and opaque films, and (B) glass microdevice with fluidic channels. .............................................. 16

Figure 9. Experimental Sequence, (A) fill up the V-shaped channel with diluted bitumen, (B) load process water into the open well to form bitumen-water interface and let it age for at least 30 minutes, (C) sprinkle some iron particles onto the water surface and let them settle down, (D) bring the magnet closer to bitumen-water interface and capture the penetration events using a high-speed camera with 20X magnification under an optical microscope..................................................... 20

Figure 10. [Left]Schematic of the glass microdevice with dimensions, and [Right] side view and top view of the glass microdevice................................................................. 20

Figure 11. Histogram of particle aspect ratio (length to width ratio). .................................................. 23

Figure 12. 3D confocal image of an iron particle. ................................................................. 23

Figure 13. The relation between drag coefficient correction factor and particle roughness factor. ................................................................................................................................. 25

Figure 14 Forces acting on a magnetic particle moving in a fluid................................................. 25
Figure 15. Relation between capillary number (Ca) and magnetic to interfacial force ratio ($\chi$). . 26
Figure 16. A particle in a steady state configuration at HMO and AQ1 interface. ..................... 28
Figure 17. A schematic diagram of particle interaction at aqueous phase and oil phase interface.
................................................................................................................................................... 29
Figure 18. No Emulsification or Outcome 0: Particle penetration across LMO - AQ2 interface,
particle velocity = 46 mm/s, particle size = 62 $\mu$m $\times$ 47 $\mu$m, recording speed = 1500 fps (t = 0 ms
is when the particle touches the interface for the first time)........................................................ 29
Figure 19. Pinch-off Emulsification or Outcome 1: Particle penetration across HMO - AQ1
interface, particle velocity = 9 mm/s, particle size = 60 $\mu$m $\times$ 41 $\mu$m, recording speed = 1000 fps
(t = 0 ms is when the particle touches the interface for the first time). (pinch-off droplets are
indicated with red arrows) ........................................................................................................ 30
Figure 20. Pinch-off and Residual Tail Emulsification or Outcome 2: Particle penetration across
LMO - AQ1 interface, particle velocity = 95 mm/s, particle size = 45 $\mu$m $\times$ 50 $\mu$m, recording speed
= 2000 fps (t = 0 ms is when the particle touches the interface for the first time). ...................... 31
Figure 21. The dependence of the outcome of particle impingement on the force ratio for (A) LMO
and (AQ1 or AQ2) interface, and (B) (LMO or HMO) and AQ1 interface ................................. 32
Figure 22. Comparison of normalized tail diameter and fractional pinch-off volume for (A)
viscosity ratio at (LMO or HMO) and AQ1 interface, and (B) interfacial tension at LMO and (AQ1
and AQ2) interface............................................................................................................... 33
Figure 23. Trends of (A) particle penetration time, and (B) normalized penetration time at mineral
oil and aqueous phase interface. ............................................................................................... 33
Figure 24. Pinch-off Emulsification or Outcome 1: [Left] Particle penetration across 67 wt%
bitumen and process water at a pH of 9.9 interface, particle velocity = 2.1 mm/s, particle size = 70
$\mu$m $\times$ 55 $\mu$m, recording speed = 200 fps, maximum pinch-off droplet size = 5.6±0.9 $\mu$m. [Middle]
Particle penetration across 50 wt% bitumen and process water at a pH of 8.3 interface, particle
velocity = 71 mm/s, particle size = 79 $\mu$m $\times$ 55 $\mu$m, recording speed = 1500 fps, maximum pinch-
off droplet size = 7.5±0.9 $\mu$m. [Right] Particle penetration across 33 wt% bitumen and process
water at a pH of 8.3 interface, particle velocity = 230 mm/s, particle size = 81 $\mu$m $\times$ 55 $\mu$m,
recording speed = 1500 fps, maximum pinch-off droplet size = 9.4±0.9 $\mu$m (t = 0 ms is when the
particle touches the interface for the first time)........................................................................... 36
Figure 25. Pinch-off and Residual Tail Emulsification or Outcome 2: (A) schematic of pinch-off
emulsion and residual tail emulsion formation, (B) particle penetration across 67 wt% bitumen and
process water at a pH of 8.3 interface, particle velocity = 7.5 mm/s, particle size = 45 µm × 61 µm, recording speed = 150 fps, maximum pinch-off droplet size = 5.5±0.9 µm, maximum residual tail droplet size = 2.8±0.9 µm, and (C) plot shows the droplet size distribution along the particle trajectory (x) for pinch-off emulsification and residual tail emulsification. (x is the distance for the unperturbed interface).

Figure 26. Pinch-off and Stretched Tail Emulsification or Outcome 2: (A) schematic of stretched tail, and (B) particle penetration across 75 wt% bitumen and process water at a pH of 9.9 interface, particle velocity = 17 mm/s, particle size = 68 µm × 48 µm, recording speed = 500 fps, maximum droplet size = 9.4±0.9 µm.

Figure 27. Pinch-off and Extended Residual Tail Emulsification or Outcome 2: (A) sequence of images for particle penetration across 67 wt% bitumen and process water at a pH of 9.9 interface, particle velocity = 13.3 mm/s, particle size = 42 µm × 67 µm, recording speed = 500 fps, maximum droplet size = 10.3±0.9 µm, (B) plot shows the droplet size distribution along the particle trajectory (x) for Outcome 2. (x is the distance for the unperturbed interface), and (C) schematic of extended residual tail emulsification.

Figure 28. Emulsification Outcomes (Bitumen and Process Water interface): The dependence of the Outcome of particle impingement on the force ratio for different bitumen dilution and process water pH. (A) the black line shows the median transition force ratio, and (B) median transition force ratio with error bars.

Figure 29. A schematic of a trail of droplets formed from residual tail emulsification.

Figure 30. A trend of normalized residual tail diameter with χ for bitumen-water system.

Figure 31. Histogram of droplets sizes in Outcome 2 for water pH, 8.3 and 9.9, and bitumen wt%, 50 and 67, grouped by the force ratio range; histogram of (A) the fractional count of the droplets (black dotted line – median droplet size, red dotted line – median ± standard deviation), and (B) fractional volume of droplets in each group (bin width = 0.94).

Figure 32. A trend of droplet size distribution (median and standard deviation) and the force ratio for (A) Outcome 2, and (B) Outcome 1. (dots represent the median of droplet size in each residual tail emulsification and the end points of the vertical lines represent median ± standard deviation).

Figure 33. Histogram of droplets formed in Outcome 2 for water pH, 8.3 and 9.9, and bitumen wt%, 50 and 67, grouped by distance intervals; histograms of (A) the fractional count of the
droplets (black dotted line – median droplet size, red dotted line – median ± standard deviation), and (B) fractional volume of droplets in each group (bin width = 0.94). Figure 34. Histogram for the normalized location of the largest droplet formed via pinch-off emulsification. [the droplet closest and farthest to the unperturbed interface is 0 and 1, respectively]. The location of the largest droplet was normalized by using the distance between the nearest and the farthest pinch-off droplets from the unperturbed interface. Figure 35. A trend of normalized residual tail diameter with $\chi$ for 50 wt% bitumen for two different particle size range: Type 1(36-55 µm) and Type 2(67-91 µm). Figure 36. Droplet size distribution for Type 1 and Type 2 particles for pH 9.9 water and 50 wt% bitumen: (A) comparison of droplet size distribution for Outcome 2 (median and standard deviation) and the force ratio, and (B) the histogram of droplets formed in all Outcome 2 cases (black dotted line represents median of droplets size). Figure 37. Satellite and primary droplets formed in Outcome 2. Particle penetration across 50 wt% bitumen and process water at a pH of 9.9 interface, particle velocity = 223 mm/s, particle size = 105 µm × 77 µm (Satellite droplets are in red dotted circles). Figure 38. Trends for particle (A) penetration time, and (B) normalized penetration time at bitumen and process water interface (penetration time normalized using particle characteristic time scale). Figure 39. Total emulsified volume to particle volume ratio as a function of $\chi$ for Outcome 1 and Outcome 2 for Type 1 particles. Figure 40. Total emulsified volume to particle volume as a function of magnetic to interfacial force for Outcome 1 and Outcome 2 for Type 2 particles (50 wt% bitumen and pH 9.9 of process water).
<table>
<thead>
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<th>Symbol</th>
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<td>drag coefficient</td>
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<tr>
<td>$C_{D,corr}$</td>
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<td>$\chi_{scep}$</td>
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<tr>
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<td>particle length, m</td>
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<tr>
<td>$\mu$</td>
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<tr>
<td>$\nu$</td>
<td>kinematic viscosity, m$^2$/s</td>
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<tr>
<td>$\Delta P$</td>
<td>pressure drop across the tubing, Pa</td>
</tr>
<tr>
<td>$Q$</td>
<td>fluid volumetric flow rate through the tubing, m$^3$/s</td>
</tr>
<tr>
<td>$r$</td>
<td>radius of the tubing, m</td>
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<td>$R$</td>
<td>particle radius, m</td>
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<tr>
<td>Re</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>$\rho_1, \rho_2$</td>
<td>density of phase 1, phase 2, kg/m$^3$</td>
</tr>
</tbody>
</table>
\( \rho_f \)  
bitumen or oil phase density, kg/m\(^3\)

\( t_{Ca} = \frac{\mu d_p}{\gamma} \)  
capillary time scale, s

\( t_p \)  
penetration time, s

\( v \)  
particle velocity, m/s

\( w \)  
particle width, m
Chapter 1
Introduction and Motivation

1.1 Oil sands overview

Alberta’s oil sands are the world’s third-largest oil reserves with proven reserves of 166 Billion barrels (bbl)[1]. Approximately 20% of Alberta’s oil sands is on the surface whereas the rest is deposited underground. Surface-mined oil sands from open pits comprise solids, bitumen, water, and salts. Oil sands undergo three steps to be converted into the final synthetic crude product – (i) Mining, (ii) Extraction, and (iii) Upgrading as shown in Figure 1. Surface-mined oil sands, containing ≈10-12 % bitumen, ≈5 % water, and ≈80-85 % solids by weight, are crushed using double roll crushers. The fines (solids smaller than 44 μm) in crushed sands can range from 4 wt% to 23 wt% and the median particle size, d_{50}, can vary between 130 and 310 μm [30]. Clark hot water extraction process is employed for bitumen extraction from crushed bituminous sands, wherein hot alkaline water is used to liberate bitumen from solids [2]. Crushed sands are mixed with hot water from tailings at a basic pH of 8.3 (achieved by the addition of NaOH), in stirred tanks, cyclo-feeders, or rotary breakers to form the bitumen slurry [3]. The bitumen slurry, ≈12% bitumen, ≈52% water and ≈36% solids by volume, density approximately 1600 kg/m³, is transported through a hydrotransport line at an average velocity of 2-5 m/s and an operating temperature of 80ºC [4]. Bitumen liberation, ablation, and lump size reduction occur in the hydrotransport line. The reduced interfacial tension of the water-bitumen interface under the alkaline conditions and the hydrophilic nature of oil-sand grains facilitate the liberation process [5]. The liberated bitumen separates from water and solids in the Primary Separation Vessel (PSV) due to gravity, and is deaerated. The deaerated bitumen froth obtained contains ~60% bitumen, ~30% water, and ~10% solids. It is diluted using naphtha or a paraffinic solvent to reduce the density and viscosity of the froth, which enhances the settling velocity of the water droplets and solid particles. The diluted froth is then sent to inclined plate settlers, cyclones, and/or centrifuges for water and particle removal to enhance bitumen recovery. The recovered water is sent back to the tailings and recycled. The diluted bitumen product is then sent to the upgrading processes, which include hydrodesulfurization, hydrocracking and coking to convert bitumen into a synthetic crude that is saleable in the open-market.
Figure 1. Schematic of synthetic crude oil (bitumen) production from oil sands using Clark hot-water extraction, froth separation, froth treatment, and upgrading process. (adapted from Masliyah et al. [3])

1.2 Motivation

A major and longstanding technological challenge faced by the oil sands industry of Alberta is the presence of water in the diluted bitumen product. Despite the cascade of processes e.g. inclined plate settling, cyclonic separation, centrifugation, etc. and chemical additives (e.g. demulsifying agents) used to recover bitumen in its purest form from the froth, the bitumen product still contains 2-3% water and 0.5-1% solids by weight [6]. Water and solids are detrimental to pipeline transportation, upgrading, and refining processes. Salts (e.g. chlorides, carbonates, sulfates, etc.) present in oil sands are dissolved in the alkaline process water during the extraction process and are, thus, also present in the residual water in bitumen. Chlorides react with hydrogen in the hydrocracking process and form hydrogen chloride (HCl). HCl acts as a catalyst poison for the coking process, and also, corrodes reactors and transportation lines. The presence of even small quantities of HCl costs millions of dollars to the oil sands industry in reactor catalyst and pipeline maintenance. The aforementioned problems can be avoided if water is less than 0.5% in the bitumen product.
To avoid the presence of water, it is necessary to first understand the morphology of water in the bitumen froth. In the literature, water in the bitumen froth is recognized to be present in the form of droplets whose sizes can be classified into three categories [6]:

(i) Type I: Free water, larger than 60 µm, separable using sedimentation
(ii) Type II: Dispersed water, 10-60 µm, separable using centrifugation
(iii) Type III: Emulsified water, smaller than 10 µm, that cannot be removed with the current operations in the industry.

Water drops belonging to the first two size categories are separable by sedimentation and centrifugation, but drops of type III are not. The droplet size distribution in bitumen froth measured in Prof. Edgar Acosta’s Laboratory at University of Toronto revealed how small the type III droplets can be. Acoustic spectrometer evaluations of a model froth diluted under mild mixing conditions showed the presence of not only micron-sized drops, but also a fraction of sub-micron droplets, which cannot be visualized in brightfield optical microscopy (see Figure 2).

![Acoustic resonance spectrometer](image)

Figure 2. Acoustic resonance spectrometer shows a bimodal distribution of sub-micrometer and micrometer size water droplets in bitumen froth, diluted under mild mixing conditions.

One of the most common approaches to remove type III water is to determine the parameter regime of process variables for which the coalescence of water droplets can be enhanced, thus enabling the removal of the larger coalesced droplets using centrifugation or inclined plate settlers. However, the type III droplets are too large for Brownian motion and too small in volume fraction to achieve an inter-drop collision rate sufficient to bring about coalescence at a reasonable rate. Moreover, even if flow in the form of gentle mixing is used to increase the number of collisions
per unit time, the interfacial moieties present in bitumen, particularly the asphaltenes, stabilize the water droplets, leading to a low efficiency of coalescence [7-12]. Due to these challenges, coalescence of water droplets in bitumen is still an area of intense, ongoing research, not only in our group, but several other groups in Canada and around the world.

Figure 3. Boundary integral simulation of a particle under a constant force penetrating through water-oil interface: (A) a particle (black dot) pushed against a drop by a force F, (B) a zoomed-in view of the penetration of the particle from water into oil.

In our group, we have adopted the alternative approach of determining the mechanisms and process conditions whereby extremely fine droplets are formed, so that the creation of such droplets may be prevented. In this thesis, it is hypothesized that extremely fine, type III droplets can form during the extraction, hydrotransport, and/or froth treatment process under turbulent flow or mixing conditions, when the solids present in process water interact with the water-bitumen interface. According to this hypothesis, when a particle with a force F impinges on the interface, upon having the minimum required energy, it may penetrate into the interface and/or form a water tail. This water tail may undergo capillarity-driven breakup to form a water-in-oil emulsion. This hypothesis is verified experimentally in this thesis using a microscale device for different bitumen dilutions, water alkalinitities, impinging forces and particle sizes. We not only visually demonstrate the formation of extremely fine water droplets during the particle penetration process, but also outline the industrially-relevant hydrodynamic and interfacial conditions where this mechanism of emulsification is likely to be manifested.

This thesis is organized as follows.
Chapter 2 discusses the existing mechanisms whereby water-in-oil emulsions can be formed. Along with the emulsification mechanisms, a discussion of the hydrodynamics of the particle penetration in the creeping flow and the inertial regime is provided.

Chapter 3 presents the experimental procedure used to test the hypothesis. It also discusses the relevance of the experimental variables to the industrial operating parameters.

Chapter 4 describes various emulsification mechanisms observed during particle penetration across a surfactant-free, mineral oil / alcohol-water mixture interface and the surfactant-rich, bitumen/water interface. The results of our experiments reveal the conditions required for emulsification, the sizes of water droplets formed, and the total emulsified volume for industrially relevant parameters: bitumen concentration, process water pH, particle size, and the force acting on the particle.

Chapter 5 summarizes the results and discussions, and provides directions for future work.
Chapter 2
Literature Review

2.1 Mechanisms for emulsification of extremely fine water droplets in bitumen

2.1.1 Spontaneous emulsification

Spontaneous emulsification has been presented as a possibility for the presence of emulsified water droplets in bitumen product. Yang et al. [13] observed spontaneous emulsification near water-bitumen interface for naphtha to bitumen ratio (N/B) < 4. This emulsification mechanism was more noticeable for N/B < 1.5 and resulted in the formation of 1-3 µm water droplets in bitumen. Although the time required to form these droplets was not investigated in depth, the maximum emulsified water content increased with a decrease in the dilution of bitumen, attaining a value 0.34% at an N/B ratio of 0.5. A similar emulsification mechanism was observed in very dilute bitumen solutions when a water-bitumen interface was subjected to area contraction [14]. Such solubilization likely takes place due to the local destabilization of the interface and the subsequent trapping of water in aggregates of surfactants found in bitumen.

2.1.2 Tip-streaming

Moyle et al. [16] define tip-streaming as “the ejection of small droplets from a liquid thread formed from the concentration gradients and the convective transport of surfactant.” The flow-induced localization of surfactants at the bitumen-water interface under a shear flow can lead to the formation of micrometer and sub-micrometer droplets in bitumen via tip-streaming [see Figure 4]. This phenomenon is not observed in a surfactant-free system. de Bruijn established that tip-streaming occurs for an optimal range of bulk surfactant concentration. Specifically, the bulk surfactant concentration must be between 10% to 90% of the maximum interfacial concentration and the viscosity ratio (dispersed phase to continuous phase viscosity) must be small (typically less than 0.1) [17][18][19]. When a surfactant concentration and hence interfacial tension gradient is established, a thin thread of the dispersed phase forms and this thread undergoes capillary instability to form droplets. The decrease in viscosity ratio allows the formation of longer and more slender threads before disintegration into droplets [20]. However, it was reported that the time required for the breakup was unaffected by viscosity ratio.
Figure 4. A schematic of tip-streaming process. Adsorption and desorption of the surfactants at the interface. Elongational flow past the droplet stretches the interface and sweeps the surfactants to generate concentration gradient, it leads to form a tip with ultralow interfacial tension. A thread is released from the tip which breaks up to form droplets. (adapted from Anna et al. [21])

Sonthalia et al. (2016), in a microfluidic hydrodynamic study, demonstrated that shear-mediated tip-streaming in the froth treatment process and froth transportation can form micrometer-sized droplets [15]. It was reported that the naphthenic acids, rather than asphaltenes, were likely the dominant surfactant-active species responsible for tip-streaming in the bitumen-water system. This was validated by showing that tip-streaming was captured for the deasphalted bitumen (no asphaltenes)-water system, but not for the deasphalted-deacidified bitumen (no asphaltenes and no acids)-water system. Tip-streaming was observed for 0.35<Ca<0.87 range for industrial process pH and bitumen dilution conditions in froth treatment process. The phenomenon did not occur for 33 wt% bitumen for either pH 8.3 or pH 9.9 of process water. The naphthenic acid concentration at the interface was not in the optimum bulk concentration range for higher bitumen dilution, and hence, concentration gradients could not be established to generate a water thread via tip-streaming. Tip-streaming was captured for 50%, 67%, and 75 wt% bitumen and either pH 8.3 or pH 9.9 system except for 50 wt% bitumen and pH 8.3 of process water. Naphthenic acid adsorption rate at the interface was higher at pH 9.9 compared to pH 8.3. Due to the high adsorption rate at pH 9.9, a concentration gradient was not established for pH 8.3 water and 50 wt% bitumen and tip-streaming was observed only for pH 9.9 water and 50 wt% bitumen. The Ca range within which tip-streaming occurred was narrower for pH 9.9. The smallest thread diameter captured was 1.5 µm, but this was limited by the optical resolution of the brightfield microscopy setup employed in the experiments i.e. smaller threads could also have formed. A thick thread formation regime was reported between steady tip-streaming and dripping/jetting regime. The two remedies provided to prevent tip-streaming were (a) to increase bitumen dilution above an S/B ratio of 1,
and (b) to add naphthenic acid or other surfactants such that the interfacial surfactant concentration saturates and a concentration gradient is not generated at the interface.

2.1.3 Satellite droplet formation

Alongside the formation of micrometer or sub-micrometer droplets via tip-streaming, satellite droplet formation during drop fracture and even during tip-streaming can also lead to fine droplets. When a drop is subjected to sufficiently large extensional hydrodynamic forces, the drop stretches and breaks up into daughter drops. The formation of the daughter drops is typically accompanied by the production of fine ligaments of the drop fluid between the daughter drops. These fine ligaments undergo further breakup into finer droplets via end pinching and/or capillary instability [22]. It has been shown that the sizes of the satellite (daughter) drops can be a few orders of magnitude smaller than the parent drop.

Satellite droplet formation is also strongly dependent on the viscosity ratio [23]. The damping of the internal axial and radial flow at higher viscosity ratios (\( \lambda > O(1) \)) leads to fewer satellite droplets. What is also interesting is that satellite drop formation is not necessarily a one-stage process; the breakup of fine ligaments can lead to the formation of even finer droplets (sub-satellite). This cascade of satellite and sub-satellite droplet formation is prevalent for low viscosity ratios. For example, Tjahjadi et al. observed upto 19 satellite and subsatellite droplets when the viscosity ratio (\( \lambda \)) was 0.01 [24]. Water-in-bitumen emulsions, particularly at the high bitumen concentrations relevant to the operating conditions in the froth treatment process, have high viscosity ratios that can lead to the formation of satellite and sub-satellite drops. Satellite drop formation is the subject of an ongoing detailed investigation in our laboratory.

2.2 Hydrodynamics of particle interaction with a liquid-liquid interface

The premise of this work is that the interaction of solids present in oil sands with the bitumen-water interface can result in the generation of extremely fine water droplets in bitumen. When a particle is pushed against an interface with force, the particle can either stay at the interface or penetrate into the interface [49]. To break through a fluid-fluid interface, the force (\( F_m \)) exerted on the particle needs to exceed a critical value (\( F_m^c \)), corresponding to the characteristic interfacial force \( \pi d_p \gamma \), as shown in Figure 5.
Several studies have been conducted to understand the interaction of solid particles with water-oil interfaces. Particle interaction at fluid-fluid interfaces under gravitational and magnetic forces have been studied to measure the force required to penetrate self-assembled particles across an interface. Jones et al. [25] presented conditions for the floating and sinking of Nylon spheres at an olive oil-water interface under the influence of gravitational force. Particles in olive oil continued to stack until the deformation caused by them was higher than the capillary length scale $l_c = \sqrt{\gamma_{12}/(\rho_2 - \rho_1) g}$. Ultimately, the stack of particles sank down and formed a raft, an aggregate of particles. Similarly, Abkarian et al. [26] conducted a macro-scale study for liquid encapsulation via capillary instability of rafts; their studies apply to the colloidal scale as well.

Particle penetration across an interface has been exploited for conformal coating and interfacial tension measurement using an in-flow microfluidic device. Paramagnetic beads penetration across water-oil interface under the influence of magnetic field were performed for microfluidic conformal coating of particles [27][28]. In a similar manner, the interfacial energy ($\sim \gamma \rho d_p^2$) required to push a particle across the interface was utilized to measure the interfacial tension of $O(10^{-5}$ N/m) to $O(10^{-4}$ N/m) [29]. An interesting observation that was reported was that paramagnetic beads (5 µm) formed water threads in the oil phase after penetration and these water threads underwent capillary instability to form sub-micrometer size droplets. This phenomenon was not, however, explored in any detail by them.

2.2.1 Creeping motion of particles at the interface

The aforementioned studies present a superficial view of the particle penetration process and its potential applications. The understanding of the penetration mechanism is vital to the subject of this work. Geller et al. [30] used the boundary integral method to study the hydrodynamics of the
motion of a rigid particle initially suspended in one fluid (Fluid A) and normally approaching an interface with a second fluid (Fluid B) under creeping flow conditions. Interfacial deformation studies under constant external body force and constant velocity were performed. In that article, two distinct modes of interface deformation were demonstrated – film drainage mode, where the thin film of Fluid A between the particle and the interface continued to drain ‘ad infinitum’, [see Figure 6(top)] and tailing mode, where the particle translated several radii beyond the initial undeformed interface yet remaining suspended in Fluid A [see Figure 6(bottom)]. The tail of Fluid A formed behind the particle was observed to thin once the particle translated a certain distance from the unperturbed interface. But they were unable to continue the simulations up to and beyond the breakup of the tail due to a limitation of the boundary integral method.

Figure 6. Schematic diagram of creeping motion of a particle near a deformable Fluid A and Fluid B interface.

In creeping flow study, only hydrodynamic forces were taken into account i.e. non-hydrodynamic interactions including van-der Waals, electrostatic interactions, etc. were neglected. For hydrodynamic interaction, three dimensionless numbers were used: viscosity ratio (aqueous to oil, $\lambda$), viscous force to capillary force ratio ($Ca$), and viscous force to buoyancy force ratio ($Cg$). For the constant velocity case, both tailing and film drainage modes were observed simultaneously. However, for constant external force, only film drainage was observed when $Ca, Cg << 1$, whereas tailing occurred only when $Ca, Cg > 0.1$. The total amount of fluid entrained was observed to depend on the relative rates of particle penetration and film drainage. At a fixed viscosity ratio, as the capillary number was increased in the simulations, the drainage rate was found to decrease and the film volume was larger, while the penetration rate and tail volume increased. The combined effects lead to entrained volumes becoming larger with $Ca$. At a fixed capillary number, as the viscosity ratio was lowered by raising the viscosity of fluid B, while both the drainage and penetration rates were reduced, penetration was slowed down more strongly than drainage. This
resulted in thinner films around the particle as it entered Fluid B, and the total volume entrained was dominated by the tail region. These important trends will be invoked in the discussions in Chapter 4.

2.2.2 Inertial settling of particles through an interface

A detailed experimental and numerical study of the inertial settling regime conducted by Pierson et al. [31][32] included details on tail breakup and emulsification. Three distinct interaction profiles for the inertial settling of particles by gravitational acceleration – steady floatation, tail formation, and tail fragmentation – were presented. The oil and aqueous phases used in the experiments were silicone oils of different viscosities and glycerol-water mixtures respectively, which allowed them to vary the viscosity ratio by four orders of magnitude. Bond number (the ratio of gravitational force to interfacial tension force on a particle), Archimedes number (Reynolds number based on gravitational velocity), density ratio, and viscosity ratio (aqueous phase to oil phase) were the dimensionless numbers explored in the analysis.

Figure 7. Inertial settling of a sphere through a deformable interface, and emulsification via end-pinching.

The details of the formation of the tail and its subsequent emulsification discussed by Pierson et al. are particularly relevant to this thesis. In tail formation, a particle pulled a column of Fluid A into the Fluid B and this fluid column kept on stretching till it pinched off. Depending on inertial stresses, the pinch-off position was located either close to the initial interface or the particle. The part of the tail closer to the unperturbed interface retracted towards it, while the part away from the unperturbed interface receded towards the particle [see Figure 7]. Pinch-off resulted in the attachment of a Fluid A droplet at the back of the particle. Generally, the attached droplet volume decreased with decreasing viscosity ratio. The droplet volume was governed by the balance between buoyancy and capillary forces, when the density difference of the fluids was significant and the viscosity ratio was less than unity. However, capillary forces and drag forces acting on the
compound body, a particle with a Fluid A blob behind it, governed the size of the attached droplet when the density difference of the fluids was negligible and the viscosity ratio was larger than unity. In the cases where a long Fluid A column was formed and the viscosity of Fluid B was equal to or greater than that of Fluid A, the column pinched off from two ends – near the initial interface and the particle. Once it pinched off, it underwent end-pinching to form a streak of primary and satellite droplets of Fluid A in Fluid B [see Figure 7(bottom)].

2.2.3 Particle penetration time

Along with the drainage behavior and the emulsification mechanism discussed in the last two sections, the amount of time a particle takes before pinch-off is also relevant to this study. Dietrich et al. [50] showed that when a particle moves from a less viscous fluid into a more viscous fluid, it slows down when it impinges onto the interface due to viscous forces and interfacial forces. They defined a penetration time or passage time as the time interval between the time a particle comes in contact with the interface to the time Fluid A neck pinches-off. The penetration time was normalized by the ballistic time \( \frac{d_p}{v} \) and an empirical correlation between normalized time and the ratio of Reynolds number and Morton number was established. It was shown that the penetration time increased with decreasing viscosity ratio. However, the impact of interfacial tension on the penetration time could not be explained due to a narrow range of interfacial tension (11.2-15.2 mN/m) used.

Similar to the passage time, the characteristic sinking time, the time taken for a particle to get completely immersed in Fluid B, was scaled as particle diameter divided by particle settling velocity [51]. The ratio of characteristic sinking time to capillary time scale was 2.39 times the non-dimensional characteristic velocity (a function of contact angle, density ratio, and Bond number). Pierson et al. [32] provided the evolution of tail neck (before pinch-off) radius as a function of penetration time. The capillary time scale was used to normalize the penetration time and it was found that the neck radius was proportional to \( (t_p - t)^{2/3} \), when \( \frac{t_p - t}{t_{Ca}} \) was \( O(1) \) or less.

2.3 Summary

In the literature, various aspects of particle penetration at liquid-liquid interfaces have been studied including floating/sinking, jet or raft formation, emulsification etc. in the inertial regime. These
experimental and numerical studies were primarily conducted for particles larger than 1 mm and surfactant-free interfaces that had interfacial tensions of the order of few tens of mN/m. Creeping motion studies have also been looked into to understand the film drainage mechanism and fluid entrainment. Microfluidic studies involving the interaction of microscale particles to develop applications pertaining to self-assembly, conformal coating, interfacial tension measurement, etc. have also been explored. These experimental microfluidic studies were conducted for surfactant-rich systems having the interfacial tension of O(.01)-O(.1) mN/m, but there was little to no emphasis on emulsification mechanisms. To the best of our knowledge, there exists no study that deals with a surfactant-rich system with interfacial tensions of orders ranging from 1 to 10 mN/m using microparticles, with emphasis on the details of the emulsification mechanism, the emulsion drop sizes and the total emulsified volume. Our work addresses this knowledge gap for the specific case of the water-bitumen system.

The focus of this thesis is the elucidation of the process of penetration of a particle suspended in water across the bitumen – process water interface under the influence of an impinging force, with particular emphasis on emulsification mechanism. Unlike the materials considered in all past experimental and theoretical investigations on this subject, the water-bitumen system is a complex, surfactant-rich system. Bitumen contains two main categories of amphiphilic, surface-active species – (i) naphthenic acids, and (ii) asphaltenes. Naphthenic acids are low-molecular-weight, surfactant-like compounds which have higher adsorption rate, higher surface activity, and undergo reversible adsorption at the water-bitumen interface [9]. On the contrary, asphaltenes are heterocyclic, aromatic, and high-molecular-weight surface-active species, which have lower surface activity, and undergo slow and irreversible adsorption at the interface [10]. Asphaltenes acquire positive and negative charge at low pH and high pH of process water, respectively, increasing the hydrophilic behavior of asphaltenes, and consequently, reducing the interfacial tension at high pH or low pH [11]. At higher pH, the interfacial tension is lower because the surface-activity of asphaltenes containing acidic residues and the adsorption rate of RCOO⁻ group of naphthenic acids are enhanced [12].

Due to the additional complexity introduced by the presence of surfactants, we also performed particle interaction and penetration experiments for a mineral oil/ aqueous-IPA (Isopropyl Alcohol) solution combination. This system was a surfactant-free model system that provided a baseline for comparison with the water-bitumen system. In a shear flow, surfactants may be
segregated at the interface by the flow, which might affect the droplet break-up and particle penetration dynamics by changing the local interfacial tension. The model system experiments using the same experimental device allowed us to evaluate the role of the surfactants in the emulsification process.

The specific aims explored in this work are as follows:

1. What are the conditions for which a microparticle penetrates through a bitumen-water interface?
2. What are the differences between the penetration processes for the surfactant-rich bitumen-water system and the surfactant-free mineral oil and water-IPA system?
3. What are the various mechanisms by which water-in-bitumen emulsions are formed during the penetration process, and what are the drop sizes and emulsified volumes resulting from each mechanism?
4. How do process variables i.e. bitumen dilution, process water pH, particle size, and the impinging force affect the particle penetration and emulsification process?
5. What are the locations in the extraction process and froth treatment, where sub-micrometer to micrometer size droplets can form due to particle penetration, and are there any potential ways to avoid this phenomenon?
Chapter 3  
Materials and Methods

3.1 Materials

Toluene (99.5%), iso-propyl alcohol (99.5%) and reagent-grade heptane (99%) were purchased from Caledon Laboratory Chemicals (Georgetown, ON, Canada), and coker feed bitumen was obtained from Syncrude Canada Ltd. (Edmonton, AB, Canada). UV-curable epoxy, Loctite 363©, and plastic spacers were procured from McMaster-Carr. Iron powder was bought from chemicalstore.com. A stack of Neodymium magnets (N52) was ordered from eBay.ca. Light Mineral Oil (LMO) and Heavy Mineral Oil (HMO) were purchased from ACP Chemicals Inc. and Fischer Scientific, respectively to conduct model system experiments.

3.2 Device fabrication

Glass microdevices were used to conduct microscale particle penetration experiments. Glass slides, 75x50 mm, were employed as the base. UV-curable epoxy, Loctite 363©, was used to bond the base glass slides with top glass slides, 2 to 7 mm width and 75 mm long. The top glass slide width, 2 to 7 mm, set the distance between the interface and the magnet. Plastic spacers (McMaster-Carr), 100 µm or 200 µm in thickness, were used to create a gap between the top and bottom glass slides, and this gap was filled up with epoxy. Bitumen is a translucent liquid and its opacity varies with solvent content and bitumen film thickness. Since we were interested in imaging the penetration of particles into bitumen solutions of fairly high concentrations, the spacer thickness and therefore the channel depth was typically set to 100 µm. For experiments that investigated the effect of particle size, the spacer was 200 µm thick for the larger particles and 100 µm for the smaller particles. A part of the top glass slide was covered with an opaque sheet cut-out in the form of a V as shown in Figure 8(A). Upon exposure to UV light, all regions except the ones masked out by the V-shaped sheet were solidified. The exposure time with UV fluorescent tube (Intertek Group plc, ~1 mW/m²) for 100 µm and 200 µm was 50 and 75 seconds, respectively. The removal of the uncured epoxy using an air gun produced a V-shaped fluidic channel between two glass slides. Once V-shaped channel was fabricated, glass boundaries were formed on 3-sides of the channel to prepare an open-channel (~1 cm x 1 cm) to contain water as shown in Figure 8(B). The glass boundaries were secured using UV-curable epoxy. Finally, the microdevices were cleaned with soap solution and iso-propyl alcohol (IPA) in a sonicator for 15 minutes each.
3.3 Hydrophobization for model system experiments

The glass microdevices were hydrophobized to prevent the wetting of aqueous-organic droplets in the V-shaped channels. This procedure was required only for the model system, i.e. mineral oil and aqueous-organic phase, experiments. Water wetting in glass channels was not observed for the bitumen-water system; therefore, the glass channels in those experiments were not hydrophobized.

To hydrophobize the glass channels, the devices were cleaned with soap-solution and IPA and rinsed with 5:1:1 mixture of water: hydrochloric acid (Sigma-Aldrich): hydrogen peroxide (Sigma-Aldrich): DI water to partially oxidize the glass surface and remove any organic residual. Corona discharge (BD20-AC, Electro-Technic Products Inc., Chicago) was used to further oxidize the glass surfaces and channels. All the devices were then immediately dipped into 5%(v/v) octadecyltrichlorosilane (Gelest, Inc., USA) in ethanol. The glass devices were kept in the solution for 6 hours such that silane chains form a covalent bond with silanol groups present on the glass surface. Finally, the excess OTS from the channels was removed using ethanol and dried using an air-gun.

3.4 Design of experimental operating parameters

3.4.1 Bitumen dilution

Due to device limitations, our experiments were restricted to room temperature; the froth treatment processes is operated at 80°C. However, recognizing from the literature review that the viscosity
ratio is a key variable in the penetration process, and that bitumen viscosity is the most sensitive variable to temperature, the dilution of bitumen was varied between concentrations of 33% to 75% by weight to simulate different viscosity ratios.

3.4.2 Solvent

On the industrial scale, naphtha is used to dilute the bitumen froth. However, due to the absence of adequate ventilation, a mixture of heptane and toluene in the volume ratio 80:20 (referred to henceforth as Heptol 80:20) was used to dilute bitumen. The volume ratio was chosen to ensure that the mixture had aromatic properties similar to Naphtha.

3.4.3 Process water composition

As explained towards the end of Section 2, the process water pH is a key operating variable, as it controls the interfacial activity of acidic surfactants in bitumen. To simulate the process conditions, two values of water pH were explored: 8.3 and 9.9.

3.4.4 Particle size

Particles present in oil sands range from a few micrometers up to 300 micrometers [33]. We conducted the experiments for two different mean particle sizes: 49 µm and 83 µm. The lower limit on the particle was set by the requirement of having a sufficiently large magnetic force for achieving particle penetration, while the upper limit was set by the inability to image the penetration process at the highest bitumen concentrations employed in the experiments.

3.4.5 Force acting on a particle

The flow conditions in the extraction process vary from one unit operation to another e.g. slurry flows in the turbulent condition in the hydrotransport line, bitumen froth flow from the primary separation vessel is laminar in nature, etc. The forces acting on the particles in the Kolmogorov scale and due to the inertial subrange eddies are different. Hence, it was vital to conduct experiments for a range of forces acting on the particles to map the possible sections of bitumen production, where particles could penetrate into the interface. We explored forces ranging from 10 nN to 1 µN.
3.5 Sample preparation

3.5.1 Particles separation

Particles present in the purchased iron powder were -80 mesh (i.e. smaller than 177 µm), but very polydisperse. Iron powder was fractionated using mesh screen (VWR International) to obtain particles in desired size ranges. The fractions used to conduct experiments for 100 µm and 200 µm channel depths were 37 µm - 62 µm (-230+400), and 62 µm - 89 µm (-170+230), respectively.

3.5.2 Bitumen solution preparation

The oil phase, bitumen solution, was prepared by diluting coker feed bitumen (Saturate, Aromatic, Resin and Asphaltene (SARA) analysis – 20.2% saturates, 30.0% aromatics, 29.5% resins and 20.3% nC5-asphaltenes) with heptol 80/20 (80%v/v heptane and 20%v/v toluene) using a wrist action shaker for 2 hours to ensure homogenized mixing. Four bitumen solutions were prepared to change the viscosity of the oil phase as shown in Table 3.1.

The viscosity of diluted bitumen solution or mineral oil was measured using Hagen-Poiseuille equation for a pressure-driven flow through a tube,

\[ \Delta P = \frac{8 \mu Q L}{\pi r^4} \] …3.1

The fluid was passed through 1 ft. long and 1/32” I.D. PFA tubing (McMaster Carr) for different pressure drop, and it was collected in a measuring cylinder. The flow rate was measured using the rise in fluid level per unit time in the measuring cylinder by applying different pressure drop (1 to 5 psi) using a pneumatic pressure transducer (Type 2000, Marsh Bellofram).

<table>
<thead>
<tr>
<th>Bitumen Concentration (wt%)</th>
<th>Solvent to Bitumen Ratio (S/B)</th>
<th>Bitumen mixture viscosity (cP)</th>
<th>Viscosity Ratio (λ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>5</td>
<td>0.2</td>
</tr>
<tr>
<td>67</td>
<td>0.5</td>
<td>30</td>
<td>0.033</td>
</tr>
<tr>
<td>75</td>
<td>0.33</td>
<td>68</td>
<td>0.015</td>
</tr>
</tbody>
</table>

3.5.3 Process water preparation

The aqueous phase, process water, was simulated by adding various salts present in water such that its properties resembled that of industrial-scale process water. The concentration of salts in
water is given in Table 3.2. This mixture yielded a pH close to 8.3. For the experiments at the higher pH, NaOH was added to this mixture to adjust the pH to 9.9. The equilibrium interfacial tensions of the process water-bitumen at the two pH values of 8.3 and 9.9 was measured previously to be 12, and 4.5 mN/m, respectively with ± 1 mN/m error [34]. These values were measured using Axisymmetric Drop Shape Analysis (ASDA) apparatus [35][36]. The variation of interfacial tension values with bitumen concentration was negligible for the range used in the experiments.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaN</td>
<td>500 ppm</td>
</tr>
<tr>
<td>NaCl</td>
<td>25 mM</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>15 mM</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>2 mM</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>0.3 mM</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>0.3 mM</td>
</tr>
</tbody>
</table>

### 3.5.4 Bitumen saturation with process water

Water drops can shrink in size with time due to dissolution in bitumen [37] or spontaneous emulsification [13][14]. This shrinkage can happen rapidly for small drops due to their larger surface area per unit volume. Since the visualization of emulsified droplets and the measurement of their sizes is critical to our work, the shrinkage of the process water droplets in the bitumen solution needs to be avoided. Therefore, the bitumen solution was saturated with the process water before using it for the experiments. The bitumen solution was mixed with pH 8.3 process water (3:1 volumetric ratio) in a vortex mixture to form water-in-bitumen emulsion and it was stored in a container for 24 hours to saturate bitumen with water. Bitumen and water mixtures were then centrifuged at 3000 rpm for 30 minutes to separate the residual water from the saturated bitumen. This saturated bitumen was used to conduct all the bitumen-water system experiments. The saturation slowed down the shrinkage process considerably, allowing us to measure the drop sizes accurately.

### 3.6 Experimental setup

The glass microdevice was positioned on an optical microscope stage (Nikon TI-Eclipse). The V-shaped channel was filled with bitumen, followed by loading the open channel with process water [see Figure 9(A-B)]. The interface was aged for 30 minutes before conducting experiments such
that the interface saturates with the surfactants in the oil phase (particularly the asphaltenes). After 30 minutes, iron particles were sprinkled on the open channel and water was stirred gently using a pipette to sink all the particles as shown in Figure 9(C). Once all the particles settled down, a stack of three neodymium N52, 1.3 mT magnetic field density magnets (see Figure 10[Right]), was manually brought closer to the interface with an impulse to pull particles towards the interface as shown in Figure 9(D). The stack of neodymium magnets (hereafter, magnet) was formed by assembling two, $1 \text{ cm} \times 1 \text{ cm} \times 0.5 \text{ cm}$, square magnets and one, $1 \text{ cm}$ diameter and $1 \text{ cm}$ length, cylindrical magnet. The same experimental sequence was followed for mineral oil and aqueous-organic mixture with the exception that the aging step was avoided.

Figure 9. Experimental Sequence, (A) fill up the V-shaped channel with diluted bitumen, (B) load process water into the open well to form bitumen-water interface and let it age for at least 30 minutes, (C) sprinkle some iron particles onto the water surface and let them settle down, (D) bring the magnet closer to bitumen-water interface and capture the penetration events using a high-speed camera with 20X magnification under an optical microscope.

Figure 10. [Left] Schematic of the glass microdevice with dimensions, and [Right] side view and top view of the glass microdevice.

We digress here briefly to explain why the magnet was brought towards the device with an impulse. Iron particles are ferromagnetic in nature and upon imposing a magnetic field on them, all the particles align themselves in the direction of magnetic field and cluster up. Therefore, if the
magnet was brought in the vicinity of the particle reservoir before the penetration experiments, upon sprinkling the particles on the open channel, they would undergo clustering [38]. This was undesirable because our interest was to understand the penetration behavior of a single particle, not a cluster.

A high-speed camera (Phantom V711, ITM Instruments Inc.) was attached to the microscope for image acquisition. The field of view was the x-y plane, captured using a 20X objective. It was adjusted to include a 200 µm region of the aqueous phase just preceding the interface, and spanned a distance of up to 800 µm in the oil phase. The videos captured using the high-speed camera had a pixel-to-size conversion of 0.94 µm/pixel. Manual fine focus adjustment was done right after penetration to capture in-focus micrometer-size droplets. Videos acquired were processed in ImageJ (https://imagej.nih.gov/ij/) [39] to quantify the particle size, the particle velocity, the penetration time of particle with the interface prior to penetration, the sizes of the emulsified droplets, and their positions relative to the initial unperturbed interface.

3.7 Forces acting on a particle

As the title of this thesis suggests, the emphasis of this work was emulsification by the penetration of particles from water into oil. We explained in Section 2.2 that a particle is required to have a minimum force such that it can overcome the interfacial force to penetrate through the interface. It was essential for the premise of this study to not only penetrate a particle through the interface but to also access higher force ranges and explore possible emulsification mechanisms. The interfacial tension range that we dealt with was O(1)-O(10) mN/m and the microparticles were in 10-100 µm range. One approach for studying particle penetration that has been employed in the past is the use of the gravitational force. The ratio of gravitational force to interfacial force is defined as Bond Number $Bo = \frac{(\rho_2 - \rho_1) R^2}{\gamma}$, and it shows that even a steel ($\rho_2 \approx 8000$ kg/m³) particle is required to be O(1) mm to penetrate through an interface of interfacial tension O(10) mN/m. Hence, gravitational force could not be used to penetrate microparticles through the water-bitumen interface.

An alternative approach would have been to provide these microparticles with a sufficiently large inertial force so as to penetrate through an interface in a microfluidic device. However, the velocities required for the inertial effects to be effective would have hindered us to form a stable
interface because Capillary numbers (Ca) corresponding to these flow velocities and the interfacial length scales were O(1) or larger. Under the influence of magnetic field, the penetration of paramagnetic beads (size - 5 µm) into interfaces of ultra-low interfacial tensions has been reported. The interfacial tensions reported in those works were two orders lower than the interest of current study. The ratio of magnetic force to interfacial force can be defined as $Bo_m \sim R^2 \chi_{scw} (\nabla B^2 / 2 \mu_0) / \gamma$. An examination of this ratio reveals that, for the interfacial tension and particle size considered in this thesis, there is a possibility of the magnetic force being sufficiently large to penetrate particles through the interface, but this requires a reasonably large susceptibility. However, the volumetric magnetic material content of the commercially available paramagnetic beads decreases with increasing the particle size, consequently, reducing the volumetric magnetic susceptibility of these beads. Therefore, there was only one option available, and that was to use ferromagnetic particles. Spherical magnetic particles would have been ideal to conduct the experiments, but only ferromagnetic iron microparticles could be procured at a reasonable price, and these were all anisotropic in shape.

Since the iron particles used were non-spherical, one of the major challenges was to accurately calculate the force acting on a particle. In the presented work, two possible methods could be employed to calculate the forces acting on the particles:

1. Given the location of the magnet relative to the device, magnetic force density could be calculated using a numerical simulation. The magnetic force acting on a particle could then be estimated by multiplying magnetic force density with particle volume.
2. The co-ordinates of the moving particle with respect to time could be used to calculate the magnetic force acting on it.

Method-1 was discarded because the magnet was not located at a constant distance from the interface. Recall that the magnet was brought closer to the interface with an impulse every time a particle penetration experiment was conducted. In the experiments, the time for particle penetration (1-100 ms) was smaller or comparable to the time required to bring the magnet towards the device. Hence, moving the magnet introduced an uncertainty factor to the distance between the interface and the magnet. The calculation described in Method-1 was tried; however, the magnetic force data obtained did not estimate the observed particle velocities. Therefore, Method-2 was selected, which used direct measurements from the experiments to deduce the force.
Although the particles were non-spherical, microscopy images showed that they could be approximated as ellipsoids. The length (x-direction) of the particle was larger than particle width (y-direction) in most of the cases (see Figure 11) Also, the wall-effects were significant because the particle size was comparable to the channel depth of 100 µm and 200 µm used in the experiments. These two observations compelled us to factor in the particle shape and the wall-effect for the magnetic force calculations. We made the following assumptions:

1. All the particles were predominantly ellipsoidal in shape, with small roughness elements (see figure 12).

2. The particle height in the z-direction was equal to the particle width (the smaller of the two length scales in the imaging plane). This was due to the restriction that only a 2D image of a particle could be captured by the camera.

3. Particles were found to be moving closer to the bottom wall due to gravitational force in the direction perpendicular to their motion. Since the particles were rough, the separation between the particle and the bottom wall could not be smaller than the scale of the asperities on the particle surface. We assumed that the separation was of the order of the roughness, and calculated the effect of a lubricating layer of fluid of this thickness on the particle mobility.

Figure 11. Histogram of particle aspect ratio (length to width ratio).

Figure 12. 3D confocal image of an iron particle.
3.7.1 Drag coefficient for non-spherical particles

G. Bagheri et al. [40] presented a general model to calculate drag coefficient for non-spherical particles at Reynolds number, \( \text{Re} < 3 \times 10^5 \). It was given by the following equation:

\[
C_D = \frac{24k_s}{\text{Re} \left( 1 + 0.125 \left( \frac{\text{Re} k_N}{k_s} \right)^{2/3} \right) + \frac{0.46k_N}{1 + 5330 \left( \frac{\text{Re} k_N}{k_s} \right)}} \quad \ldots 3.2
\]

The various parameters in the above equations are defined below:

\[
\text{Re} = \frac{\rho_p v d_p}{\mu}, \quad \ldots 3.3
\]

\[
d_p = (w^2 l)^{1/3}, \quad \ldots 3.4
\]

\[
k_s = \left( f_s^{1/3} + f_s^{-1/3} \right)/2, \quad \ldots 3.5
\]

\[
k_N = 10^{\alpha \left[ -\ln (f_s/\alpha) \right]}, \quad \ldots 3.6
\]

\[
\alpha = 0.45, \quad \ldots 3.7
\]

\[
f_s = (w/l)^{1/3}, \quad \ldots 3.8
\]

\[
f_N = w/l. \quad \ldots 3.9
\]

3.7.2 Drag Coefficient Correction to Incorporate Wall-Effect

As mentioned earlier, the third assumption was that the distance between the bottom of the particle and the bottom wall can be approximated to be the particle roughness. According to lubrication theory, the drag experienced by a sphere of diameter \( d_p \) moving a distance \( \varepsilon d_p / 2 \) from a rigid plane wall [41][42] can be calculated from the corrected drag coefficient,

\[
\frac{C_{D,\text{corr}}}{C_D} = \frac{8}{15} \ln \left( \frac{1}{\varepsilon} \right) + \frac{64}{375} \varepsilon \ln \left( \frac{1}{\varepsilon} \right). \quad \ldots 3.10
\]

For our purposes, \( \varepsilon \) is a measure of the roughness on the particle surface, and was deduced from confocal imaging to be about 10%. Fortunately, while the surface roughness is large, the dependence of the correction on roughness is logarithmic, and hence, weak [see Figure 13].
3.7.3 Magnetic Force on a Particle

Once we calculate drag force acting on a particle, the net force can be defined as:

$$F_{net} = F_{mag} - F_{drag},$$  \hspace{1cm} \ldots 3.11$$

where $F_{net}$, $F_{mag}$, and $F_{drag}$ is the net force, magnetic force, and drag force, respectively, acting on the particle as shown in Figure 14. According to Newton’s second law,

$$mv \frac{dv}{dx} = F_{net} = F_{mag} - \frac{1}{2} C_{D, corr} \rho_f v^2 \frac{\pi d_p^2}{4}. \hspace{1cm} \ldots 3.12$$

For the force range within which these experiments were conducted, we found that $mv \frac{dv}{dx} \ll F_{drag}$, suggesting that viscous damping is large enough to neglect inertial effects. Therefore, the magnetic force acting on the particles was directly deduced as:

$$F_{mag} = \frac{1}{2} C_{D, corr} \rho_f v^2 \frac{\pi d_p^2}{4}. \hspace{1cm} \ldots 3.13$$

Recall that we are not only interested in the absolute magnitude of the force pushing the particle across the interface, but also how strong this force is relative to the interfacial force. The interfacial
force acting on a particle when it penetrates depends on the interfacial tension and its width, not the effective diameter. The interfacial force depends on the width rather than the effective diameter because the maximum length of the interface contact line at the particle is given by $\pi w \gamma$. Therefore, normalized force can be given as:

$$\chi = \frac{F_{\text{mag}}}{F_i} = C_{D,\text{cor}, \rho} \gamma v^2 \frac{d_i^2}{8 \gamma w} \quad \ldots 3.14$$

Equation number 14 provides the magnetic force to interfacial force ratio ($\chi$). It is represented as either “Magnetic Force/Interfacial Force” or “the force ratio” or simply as $\chi$ in the later sections. As shown in Figure 15, capillary number (Ca) is proportional to the force ratio i.e. Ca can be alternatively used as the force ratio with a prefactor (0.16).

![Figure 15. Relation between capillary number (Ca) and magnetic to interfacial force ratio ($\chi$).](image)

### 3.7.4 Error Analysis

The force ratio values were calculated using experimentally determined terms, and therefore, there was some error associated with its calculation. The force ratio in equation 3.14 could also be written as follows:

$$\chi = \frac{F_{\text{mag}}}{F_i} = \phi \frac{v d_i}{8 \gamma w} \quad \ldots 3.15$$

where $\phi$ was a term associated with the drag force calculation for a randomly-shaped particle. Based on the formula for the force ratio, the propagation error was deduced as
\[
\frac{\Delta \chi}{\chi} = \frac{\Delta \phi}{\phi} \pm \frac{\Delta \nu}{\nu} \pm \frac{\Delta d_p}{d_p} \pm \frac{\Delta \gamma}{\gamma} \pm \frac{\Delta w}{w}, \quad \cdots 3.16
\]

The error associated with each term was \( \frac{\Delta \phi}{\phi} = 0.01 \); \( \frac{\Delta \nu}{\nu} = \frac{1}{50} \); \( \frac{\Delta d_p}{d_p} = \frac{1}{50} \); \( \frac{\Delta \gamma}{\gamma} = \frac{1}{12} \); \( \frac{\Delta w}{w} = \frac{1}{50} \).

Based on these values, the maximum average relative error in the calculation was found to be 31%.

The standard deviation of residual tail diameter was used to find out the variability in the data. This force ratio was segregated into the groups of bin width 0.1 starting from zero i.e. the bins were e.g. 0-0.1, 0.1-0.2, 0.2-0.3, etc. The ratio of standard deviation to median of various properties was calculated for each of these bins wherever there were more than 2 or more number of data points. The summary of these ratios is listed in the following Table 3.3.

<table>
<thead>
<tr>
<th>Values in %</th>
<th>Force Ratio</th>
<th>Particle Diameter</th>
<th>Residual Tail Diameter / Particle Diameter</th>
<th>Residual Tail Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>0.3</td>
<td>0.5</td>
<td>0.8</td>
<td>3.0</td>
</tr>
<tr>
<td>Maximum</td>
<td>21.4</td>
<td>16.2</td>
<td>60.3</td>
<td>51.9</td>
</tr>
<tr>
<td>Median</td>
<td>3.2</td>
<td>8.3</td>
<td>16.8</td>
<td>19.9</td>
</tr>
<tr>
<td>Average</td>
<td>5.1</td>
<td>8.3</td>
<td>19.3</td>
<td>20.8</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>5.2</td>
<td>4.1</td>
<td>13.5</td>
<td>12.4</td>
</tr>
</tbody>
</table>

The standard deviation of the force ratio required for transition from Outcome 0-1 and 1-2 [defined in Section 4.1.1 and 4.2.2] was an alternative way to find out the variability in the data. The ratio of standard deviation to median of force ratios for various cases is shown in Table 3.4. The average of the standard deviation to median ratio of \( \chi \) was 23.4%.

<table>
<thead>
<tr>
<th>Bitumen wt%</th>
<th>pH 8.3</th>
<th>9.9</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Outcome 0-1</td>
<td>Outcome 1-2</td>
</tr>
<tr>
<td>33</td>
<td>42.9</td>
<td>6.6</td>
</tr>
<tr>
<td>50</td>
<td>26.4</td>
<td>20.4</td>
</tr>
<tr>
<td>67</td>
<td>39.0</td>
<td>30.5</td>
</tr>
<tr>
<td>75</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Chapter 4
Results and Discussions

In this section, the particle penetration behavior for the surfactant-free model system, mineral oil and aqueous-organic solution, is discussed first, followed by the surfactant-rich, bitumen solution-process water system.

4.1 Model system – mineral oil and aqueous-organic solution

4.1.1 Particle Penetration across mineral oil and aqueous-organic solution interface

Light mineral oil (LMO) or heavy mineral oil (HMO) were used as the oil phase. A mixture of water and IPA was used as the aqueous-organic phase, hereafter aqueous phase. Water and IPA were used in either 1:2 or 2:1 volumetric ratio (AQ1 and AQ2, respectively). When an iron particle reached the interface under the influence of the magnetic field, the particle did not always penetrate the interface. An example of a case when the particle did not penetrate the interface is shown in Figure 16; both experimental and theoretical research in the past have confirmed this steady state configuration [43][44]. However, our interest lies in the fate of the interface after the particle penetrates it.

Under a sufficiently strong magnetic force, the particle, coated by an aqueous film [Figure 17 (top)] continued to move several radii into the oil phase and formed a neck [see Figure 17(center)]. A few different outcomes were observed upon the evolution of this neck. In some cases, the neck behind the particle pinched off, and the two parts of the aqueous tail relaxed back without any emulsification; we refer to this fate as Outcome 0 or “no emulsification” [see Figure 18]. In other cases, the part of the tail post pinch-off that was still attached to the interface fragmented to produce fine droplets of the aqueous phase in the oil; we refer to this phenomenon as “pinch-off emulsification” or Outcome 1 [see Figure 19].

Figure 16. A particle in a steady state configuration at HMO and AQ1 interface.
Figure 17. A schematic diagram of particle interaction at aqueous phase and oil phase interface.

Figure 18. *No Emulsification or Outcome 0*: Particle penetration across LMO - AQ2 interface, particle velocity = 46 mm/s, particle size = 62 µm × 47 µm, recording speed = 1500 fps (t = 0 ms is when the particle touches the interface for the first time).

Once pinch-off occurs, the particle has an aqueous film coated around it and/or an aqueous fluid blob behind the particle [see Figure 19]. As the particle translates towards the magnet, the aqueous fluid film around the particle is convected to the back of the particle, and consequently either establishes a new blob or enlarges the existing one. When a critical force depending on the blob size, fluid properties and interfacial conditions is exceeded, a streak of droplets is left behind as a trail along the trajectory of the particle. Emulsification in this fashion is termed as “residual tail emulsification”. It was also observed that residual tail emulsification always ensued after pinch-
off emulsification. Therefore, we defined **Outcome 2** as “pinch-off and residual tail emulsification” [Figure 20].

4.1.2 **Classification of emulsification type**

Data obtained for particle penetration was classified based on the emulsification conditions defined in the previous section [see Figure 21]. For a particle that was lodged at the interface in a steady configuration (no penetration), the magnetic force acting on the particle was not quantifiable. This was because the area of interest for image acquisition was set predominantly as the oil phase, and consequently, the frames required to reliably quantify particle motion in the aqueous phase were unavailable. For the two particle sizes employed in the experiments, the minimum force to penetrate into the LMO-AQ2 interface was about 0.2. For pinch-off emulsification, for all the oil phases and the aqueous phases employed in the experiments, a force ratio greater than about 0.4 was required. When the oil phase was LMO [see Figure 21(A)], the minimum force ratio for pinch-off emulsification was fairly insensitive to interfacial tension and particle size within the experimental error.
Figure 20. Pinch-off and Residual Tail Emulsification or Outcome 2: Particle penetration across LMO - AQ1 interface, particle velocity = 95 mm/s, particle size = 45 µm × 50 µm, recording speed = 2000 fps (t = 0 ms is when the particle touches the interface for the first time).
Figure 21. The dependence of the outcome of particle impingement on the force ratio for (A) LMO and (AQ1 or AQ2) interface, and (B) (LMO or HMO) and AQ1 interface

### 4.1.3 Effect of viscosity

The oil phase, LMO or HMO, with the aqueous phase, AQ1, were used to study the effect of viscosity ratio on emulsification. The viscosities of AQ1 and AQ2 were nearly the same: 2.2(±0.1) cP [45].

<table>
<thead>
<tr>
<th>Oil phase</th>
<th>Aqueous-organic phase</th>
<th>Viscosity ratio (λ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMO</td>
<td>AQ1</td>
<td>0.15</td>
</tr>
<tr>
<td>LMO</td>
<td>AQ2</td>
<td>0.15</td>
</tr>
<tr>
<td>HMO</td>
<td>AQ2</td>
<td>0.04</td>
</tr>
</tbody>
</table>

The minimum force ratios required to initiate Outcome 1 (pinch-off emulsification) and Outcome 2 were higher for HMO than LMO [see Figure 21(B)]. For example, the minimum force ratios required for Outcome 2 for HMO and LMO were about 1.9 and 1.4, respectively. This trend could be related to the observations of Geller et al. [30] discussed in section 2.2.2. For a fixed force ratio, as the viscosity ratio is reduced, the penetration process is slowed down more strongly than film drainage, and hence, the tail formed before the pinch-off is thinner for the more viscous oil phase [see Figure 22(A)]. This implied the existence of a force ratio for which the tail was pinched off and produced drops for the less viscous phase, but did not produce any (visible) drops for HMO (χ < 0.4). It is noteworthy that for the same force ratio, the fractional pinch-off volume (pinch-off emulsion volume to particle volume) was smaller for lower viscosity ratio (HMO) fluid. In other words, a higher force ratio was required for HMO-AQ1 interface to obtain tail of the width
same as that of LMO-AQ1 interface. The higher force ratio required for residual tail emulsification for HMO relative to LMO could be explained using the same arguments.

Figure 22. Comparison of normalized tail diameter and fractional pinch-off volume for (A) viscosity ratio at (LMO or HMO) and AQ1 interface, and (B) interfacial tension at LMO and (AQ1 and AQ2) interface.

The minimum observable size of the drops produced by pinch-off was limited by the optical resolution. It is possible that droplets finer than 1.9 µm ± 0.9 µm (2 pixels ± 1 pixel) were formed in Outcome 0, but those could not be resolved, and therefore, were labeled as Outcome 0 rather than Outcome 1.

Figure 23. Trends of (A) particle penetration time, and (B) normalized penetration time at mineral oil and aqueous phase interface.

Shown in Figure 23 is the particle penetration time, which is the time elapsed from the instant of particle impingement on the interface to the instant of tail pinch off. As the viscosity ratio was decreased, for the same value of $\chi$, the particle penetrated HMO-AQ1 interface more slowly than
4.1.4 Effect of interfacial tension

The magnetic force range applied on the particle was 0.26 µN to 4.9 µN and 0.79 µN to 8.0 µN for LMO-AQ1 \((\gamma = 4.2 \text{ mN/m})\) and LMO-AQ2 \((\gamma = 14.5 \text{ mN/m})\), respectively. The collapse of the trends in Figure 21(A) for the two systems with different interfacial tensions but the same viscosity ratio (LMO) suggested that the transition from Outcome 0 to 1 and 1 to 2 occurred for forces lower by a factor of approximately 3.5 for the LMO-AQ1 compared to the LMO-AQ2. Also, normalized tail diameter and fractional pinch-off volume for AQ1 and AQ2 overlapped within the experimental error [see Figure 22(B)] i.e. for a given value of \(\chi\), the normalized tail diameter was same for either interfacial tension. This indicated that these two systems were dynamically similar. The minimum force ratio to attain Outcome 2 for AQ1 was 1.4 and it was not captured for AQ2 due to lower entrainment rate at the same force. Due to dynamic similarity, we expect that Outcome 1 to Outcome 2 transition for AQ2 occurs at a force ratio of 1.4.

In summary, when a particle penetrated a surfactant-free interface, three distinct outcomes were observed – no emulsification, pinch-off emulsification, and pinch-off and residual tail emulsification. Prior to pinch-off, the time spent by the particles at the HMO-AQ1 interface was higher than the LMO-AQ1 interface. The minimum force ratio required for Outcome 1 and Outcome 2 was higher at lower viscosity ratios, but relatively independent of interfacial tension. Thus, the force ratio and the viscosity ratio were sufficient to completely characterize the behavior of the clean interface system, which is consistent with the theoretical work done by Geller et al. (1986).

4.2 Bitumen system – bitumen solution and process water

4.2.1 Particle penetration across bitumen solution and process water interface

Similar to the surfactant-free system, pinch-off emulsification and residual tail emulsification were also observed for the surfactant-rich bitumen system. Before delving into the quantitative details of the penetration process for the bitumen system, the qualitative similarities and differences
between the surfactant-free and surfactant-rich system are discussed. Figure 24 shows pinch-off emulsification (Outcome 1) for 33, 50, and 67 % diluted bitumen and process water. These are qualitatively similar to the pictures for the surfactant-free system in Figure 19. The timestamps on the images reveal that penetration takes a significantly longer time for a bitumen concentration of 67%. While the $\chi$ values for the experiments in Figure 24 were not the same and a comparison, therefore, would be inexact, the trend of slower penetration was valid for all occurrences of Outcome 1 for the different bitumen concentrations, and was also consistent with our clean interface studies. 67 wt% bitumen had a viscosity that was significantly higher than the viscosities of 33 and 50% bitumen, and consequently, the penetration process was slower. Note that for the experiments performed at the bitumen concentration of 75%, however, the details of pinch-off emulsification events could not be recorded due to the high opacity of 75 wt% bitumen. The high intensity of light required for these experiments implied that the region in the images close to the interface was invariably flooded with light; the particle interaction with the interface could not, therefore, be captured prior to pinch-off. The flooding of light had two implications. First, when a particle penetrated through the interface and if there was no residual tail emulsification then no emulsification and pinch-off emulsification could not be distinguished. Because pinch-off droplets formed could not be seen due to the flooding, and consequently, we could not obtain droplet size data from pinch-off emulsification. Second, as ‘no emulsification’ and pinch-off emulsification could not be distinguished, the force ratio required for the transition from Outcome 0 to 1 could not be quantified.

An example of the images of the residual tail emulsification process or Outcome 2 for a particle penetrating across 8.3 pH process water and 67 wt% bitumen interface is shown in Figure 25. The images show a distinctly different feature compared to the corresponding images for the clean interface model system in Figure 20. The water entrained by the particle was relegated to its back and deformed into a conical shape, and fine droplets were dispensed from the tip of this cone. This particular mode of residual tail emulsification was reminiscent of the phenomenon of tip-streaming (Figure 4 in Section 2), wherein surfactants present at an interface were swept towards the tip of a sheared drop and locally reduced the interfacial tension to ultralow values there, leading to the drawing of an extremely fine thread from the tip. The finest droplets captured by the imaging system were again 1.9± 0.9 µm.
Figure 24. Pinch-off Emulsification or Outcome 1: [Left] Particle penetration across 67 wt% bitumen and process water at a pH of 9.9 interface, particle velocity = 2.1 mm/s, particle size = 70 µm × 55 µm, recording speed = 200 fps, maximum pinch-off droplet size = 5.6±0.9 µm. [Middle] Particle penetration across 50 wt% bitumen and process water at a pH of 8.3 interface, particle velocity = 71 mm/s, particle size = 79 µm × 55 µm, recording speed = 1500 fps, maximum pinch-off droplet size = 7.5±0.9 µm. [Right] Particle penetration across 33 wt% bitumen and process water at a pH of 8.3 interface, particle velocity = 230 mm/s, particle size = 81 µm × 55 µm, recording speed = 1500 fps, maximum pinch-off droplet size = 9.4±0.9 µm (t = 0 ms is when the particle touches the interface for the first time)

The features of Outcome 2 for 75% bitumen were distinctly different from those at lower bitumen concentrations. As shown in Figure 26, the conical nature of the water-bitumen behind the particle was much less pronounced, and thicker threads were observed. The water droplets in 75 wt% bitumen were a result of the disintegration of this thick thread. The preponderance of thick threads at very high bitumen concentrations is another feature that is consistent with the work of Sonthalia et al.(2016).
Figure 25. Pinch-off and Residual Tail Emulsification or Outcome 2: (A) schematic of pinch-off emulsion and residual tail emulsion formation, (B) particle penetration across 67 wt% bitumen and process water at a pH of 8.3 interface, particle velocity = 7.5 mm/s, particle size = 45 µm × 61 µm, recording speed = 150 fps, maximum pinch-off droplet size = 5.5±0.9 µm, maximum residual tail droplet size = 2.8±0.9 µm, and (C) plot shows the droplet size distribution along the particle trajectory (x) for pinch-off emulsification and residual tail emulsification. (x is the distance from the unperturbed interface).

In the surfactant-free system, emulsification was classified into three categories. Emulsification for the surfactant-rich bitumen system for Outcome 1 is shown in Figure 24 and Outcome 2 is shown in Figures 25, 26, and 27. Based on the observations for the bitumen-water system, sub-classes of Outcome 2 need to be defined. In some cases, when a particle penetrated through the interface [see Figure 26], the tail formed did not undergo pinch-off and kept on stretching, until it disintegrated. A schematic of this scenario is shown in Figure 26(A), and is referred by us as stretched tail emulsification. Outcome 2 also had cases that were intermediate to the two extremes of tip-streaming and thick thread formation as shown in Figure 27(C); we labeled those cases as
extended residual tail emulsification. An experiment where extended residual tail emulsification occurred is shown in Figure 30(A). Here, the particle penetrated through the interface, underwent pinch-off, and a long, extended residual tail was formed. When this mode of breakup occurred, droplets resulting from pinch-off emulsification and residual tail emulsification did not have a discernible gap between them, and hence could not be distinguished.

The aforementioned two observations and therefore updates to the definition occurred for larger bitumen viscosities and higher particle velocities. One possible explanation for the formation of these long residual tails could be the longer time capillary breakup time scale \((1 + \lambda) \mu d_{\text{tail}}/\gamma\). However, we could not substantiate this argument quantitatively with the experimental data because the local interfacial tension values could not be ascertained. A detailed numerical study including the hydrodynamics, mass transfer, and adsorption desorption kinetics for a surfactant-rich system is required to find out the thread breakup time scale.

Figure 26. *Pinch-off and Stretched Tail Emulsification or Outcome 2*: (A) schematic of stretched tail, and (B) particle penetration across 75 wt% bitumen and process water at a pH of 9.9 interface, particle velocity = 17 mm/s, particle size = 68 µm × 48 µm, recording speed = 500 fps, maximum droplet size = 9.4±0.9 µm.
Figure 27. *Pinch-off and Extended Residual Tail Emulsification or Outcome 2*: (A) sequence of images for particle penetration across 67 wt% bitumen and process water at a pH of 9.9 interface, particle velocity = 13.3 mm/s, particle size = 42 µm × 67 µm, recording speed = 500 fps, maximum droplet size = 10.3±0.9 µm, (B) plot shows the droplet size distribution along the particle trajectory (x) for Outcome 2. (x is the distance from the unperturbed interface), and (C) schematic of extended residual tail emulsification.

4.2.2 Emulsification outcomes

Emulsification conditions were classified based on various outcomes described in earlier sections. Similar to the clean-interface systems, increasing the force ratio caused the emulsification mode to transition from Outcome 0 to 1 to 2, but the actual values of the force ratio at which the transitions occurred were different. The smallest force ratio required to observe particle penetration across mineral oil-aqueous phase interface was 0.2. But for the water-bitumen system, at a force ratio of 0.2, surprisingly, pinch-off emulsification was observed. In other words, under similar dynamic conditions of force ratio and viscosity ratio, emulsification appeared to be easier for the bitumen-water system as compared to the mineral oil-water system. A possible explanation for this observation is that we employed the equilibrium interfacial tension for the calculation of
Figure 28. Emulsification Outcomes (Bitumen and Process Water interface): The dependence of the Outcome of particle impingement on the force ratio for different bitumen dilution and process water pH. (A) the black line shows the median transition force ratio, and (B) median transition force ratio with error bars.

the force ratio for the bitumen-water system. In spite of aging the interface prior to the start of the experiment, note that the interface stretches continuously during the penetration process and creates a new water-bitumen interfacial area that can have lower the concentration of interfacial species. There is a natural driving force, therefore, for surfactants in the bulk bitumen phase to adsorb to the newly created interface. An additional consideration is that the time scales of the
penetration process in our experiments ranged between a few milliseconds to hundreds of milliseconds. The surfactants that are capable of adsorbing to the interface over such short time scales are likely the naphthenic acids in bitumen and not the asphaltenes, and it is well known that naphthenic acids can reduce the interfacial tension strongly [11][12]. It is highly likely, therefore, that the dynamic interfacial tension at the time of penetration was smaller than the equilibrium interfacial tension by approximately an order of magnitude as suggested by our observations. This strong reduction of interfacial tension at such short time scales is currently being confirmed via dynamic interfacial tension measurements in our group.

4.2.3 Residual tail diameter

The approach used to quantify the average residual tail diameter for Outcome 2 is discussed. During an experiment when a particle produces droplets from a residual tail, the trail of drops was not always in focus. Since a slightly out-of-focus residual tail can introduce large errors in the residual tail diameter measurement, the captured image of the residual tail was not used to infer the tail diameter. Instead, the particle was allowed to pass the field of view, and the focus was adjusted to see the emulsified droplets clearly. The average tail diameter \( d_i \) of the residual tail was then back-calculated by summing up the volume of the observed emulsified drops using the following equations:

Average Cross-sectional Area of the Residual Tail \( A = \frac{1}{2} \left( \frac{\pi}{6} a_1^3 + \frac{\pi}{6} a_n^3 \right) + \sum_{i=2}^{n-1} \frac{\pi}{6} a_i^3 \), \hspace{1cm} ...4.1

Residual Tail Diameter \( d_i = \sqrt{\frac{4A}{\pi}} \). \hspace{1cm} ...4.2

Figure 29. A schematic of a trail of droplets formed from residual tail emulsification

Here, \( a_i \) is the diameter of the \( i^{th} \) droplet, and \( d_i \) is the distance between \( i^{th} \) and \( i+1^{th} \) droplet. A few notes of caution pertaining to the calculation of \( d_i \) are in order here. First, these droplets were
restricted to a distance of 600-800 µm from the initial unperturbed interface. This limitation was due to the 800 µm width of the frame; the droplets further downstream were not taken into account.

Second, for the Outcome 2 experiments at lower bitumen concentrations and smaller force ratios, it was possible to clearly distinguish the drops produced by pinch-off emulsification and residual tail emulsification, as a prominent gap was observable between the two sets of drops in the images. However, the distance between these two sets of drops decreased with increasing force ratio, bitumen viscosity or both, making it difficult to distinguish between the two sets, particularly when extended residual tails and stretched tails were observed (see Figure 26 and 27). In such scenarios, the emulsified droplets including the ones produced via pinch-off emulsification were labeled as residual tail emulsification. This was a reasonable approximation because, even for the cases where these two sets could be differentiated, the droplets produced by residual tail emulsification dominated the total number and volume (>70%).

For the experiments conducted with Type 1 (36-55 µm) particles, the residual tail diameter in bitumen phase was smaller than 10 µm. The average residual tail diameter was normalized using the effective particle diameter. The effective particle diameter was used instead of particle width because the volume of water in the film around a particle was related to its surface area and the volume of the liquid blob was related to the film volume. A plot of the normalized residual tail diameter, $d_t/d_p$, against the force ratio ($\chi$) is shown in Figure 30.

![Figure 30. A trend of normalized residual tail diameter with $\chi$ for bitumen-water system](image-url)
For the values of $\chi$ corresponding to the inception of the residual tail emulsification regime, notwithstanding the variability in the measurements, the normalized diameter stayed between 0.02 to 0.04. This suggested that if a 50 µm particle impinged on the interface and formed a residual tail, its diameter could be as small as 1 to 2 µm. Interestingly, the normalized tail diameters for pH 9.9 and pH 8.3 overlapped in the range of force ratios shared by the data sets. This should be explored further in the future using numerical simulations.

### 4.2.4 Water droplets size distribution

The normalized residual tail diameter had significant variability as shown in Figure 33. Ideally, we would have plotted histograms for a fixed $\chi$ value and bitumen dilution to compare droplet size distribution for different process water pH. However, due to the variability in the data, a reasonable comparative analysis could not be produced for a fixed $\chi$ value. Therefore, histograms of the droplets sizes were plotted for three groups of $\chi$ value: Range 1, Range 2, and Range 3. These three groups were classified based on the force ratio for residual tail emulsification for pH 8.3 and pH 9.9 of process water. Range 1 was the force ratio range where residual tail emulsification was observed for pH 8.3 of process water only. Range 2 was the force ratio range where residual tail emulsification was observed for both pH 8.3 and pH 9.9 of process water. Range 3 was the force ratio range where residual tail emulsification was observed for pH 9.9 of process water. Based on the classification, the $\chi$ values for Range 1, Range 2, and Range 3 for a bitumen concentration of 50% bitumen were $\chi < 0.4$, $0.4 < \chi < 0.8$, and $\chi > 0.8$, respectively. Similarly, the $\chi$ values 67% bitumen were $\chi < 0.15$, $0.15 < \chi < 0.35$, and $\chi > 0.35$, respectively. Histograms of the droplet size frequency and fractional volume for particle penetration events in the different force ranges are shown in Figure 31 for different bitumen concentrations and water pH. The histogram of droplet size distribution is right-skewed. The median and standard deviation of the droplet size was calculated by taking the logarithm of droplet size i.e. lognormal method such that the right-skewed histogram could be uniformly distributed. The same method was used to calculate the median and standard deviation for rest of the droplet size distributions reported. The smallest droplets resolved by the optical resolution of the microscope were 1.9± 0.9 µm. However, due to higher opacity and low contrast for 75wt% bitumen, the smallest droplets that could be resolved were 2.8±0.9 µm. Smaller droplets were likely present but the imaging was limited by the optical resolution. Based on the data presented in Figure 31(A) and Figure 32 (A), it appears that the median droplet size was fairly unaffected by the process water pH, $\chi$ range and
bitumen concentration, i.e. the demarcation between the numbers of the large and small drops occurred at approximately the same drop size of about 4 to 5 µm. However, the spread of sizes about the median size depended on the force ratio, particularly for the larger force ratios and high pH, where it increased strongly (see Figure 32 (A)). This trend of the spread is elicited more clearly in the fractional volume distributions in Figure 31(B), because the volume of a droplet is a cubic function of droplet size e.g. a droplet of size 10 µm has the same volume as that of 1000 droplets of 1 µm size (note that the median size remains the same). While the number of droplets larger than 7 µm was insignificant, the presence of even a single large droplet contributed significantly to the total emulsified volume and skewed the fractional volume distribution [see Figure 31(B)]. The largest spreads in the distributions were observed for Range 3 of the force ratios and a pH of 9.9. The high variance in the droplet size was a result of the accompaniment of small satellite droplets with the larger primary droplets. What is also noteworthy is that whenever satellite drops were formed, the smallest of these were always in the 2 – 3 µm size range (close to our lowest observable sizes), irrespective of χ value.

Figure 31. Histogram of droplet sizes in Outcome 2 for water pH, 8.3 and 9.9, and bitumen wt%, 50 and 67, grouped by the force ratio range; histogram of (A) the fractional count of the droplets (black dotted line – median droplet size, red dotted line – median ± standard deviation), and (B) fractional volume of droplets in each group (bin width = 0.94).
Figure 32. A trend of droplet size distribution (median and standard deviation) and the force ratio for (A) Outcome 2, and (B) Outcome 1. (dots represent the median of droplet size in each residual tail emulsification and the endpoints of the vertical lines represent median ± standard deviation).

The droplet size distribution for Outcome 2 at various distance intervals from the initial unperturbed interface provided a comparative analysis of the size variation along the particle trajectory [see Figure 33]. The experiments for particle penetration were conducted approximately equal magnetic force range for either pH or bitumen wt%. The histograms compare the droplet size distribution for process water of pH 8.3 and 9.9, and bitumen dilution of 50 and 67 wt% in the same magnetic force range. The droplet size variance was smaller for pH 8.3 in comparison with
pH 9.9 because $d_r$ for pH 9.9 was higher at the same force. The likelihood of the formation of $1.9 \pm 0.9 \mu m$ was higher for pH 8.3 in the same force range. The droplet size variance was higher near the initial interface and it decreased as the particles moved away from the initial interface. The same was observed for two individual penetration events [see Figure 25(C) and 27(B)]. A significant number of droplets in 0-200 $\mu m$ interval formed via pinch-off emulsification. The largest droplet formed by pinch-off emulsification was near the unperturbed interface in the 0-60% normalized length of the pinch-off tail [see Figure 34].

Figure 33. Histogram of droplets formed in Outcome 2 for water pH, 8.3 and 9.9, and bitumen wt%, 50 and 67, grouped by distance intervals; histograms of (A) the fractional count of the droplets (black dotted line – median droplet size, red dotted line – median ± standard deviation), and (B) fractional volume of droplets in each group (bin width = 0.94).
4.2.5 Effect of bitumen dilution and process water pH

The minimum force ratio required for the transition from Outcome 1 to Outcome 2 decreased from 33 wt% to 67 wt% bitumen and the opposite trend was observed for 67 wt% to 75 wt% bitumen [see Figure 28]. This trend was observed for both pHs of process water, and was also observed for the lowest force ratio to observe Outcome 1.

The residual tail formation was dependent on two competing effects: viscous and interfacial. The viscous effects were dominant for 75% bitumen, whereas, the interfacial effect dominated 33% to 67% bitumen concentration. The viscosity of bitumen solution increased non-linearly with bitumen concentration and decreased the water film thickness around the particle. (a detailed explanation has been provided in Section 4.1.3 and 4.2.1). The higher bulk concentration of surfactants, especially, naphthenic acids, influenced the concentration gradient at the back of the particle. Generally, increasing the bulk concentration aids the concentration gradient generation due to higher surfactant adsorption rate, however, on increasing bitumen concentration, this effect did not grow as strongly as the viscous effects due to the non-linear behavior of bitumen viscosity for the bitumen-water system.

The minimum force required for Outcome 2 at a pH of 9.9 was higher than that for a pH of 8.3. As mentioned in the literature review, the adsorption rate of naphthenic acids is higher at a pH of 9.9. Hence, a higher force ratio was required to generate concentration gradients and droplet generation via tip-streaming. However, the explanations provided for Outcome 1 to 2 transition could not be explain Outcome 0 to 1 transition.

Figure 34. Histogram for the normalized location of the largest droplet formed via pinch-off emulsification. [the droplet closest and farthest to the unperturbed interface is 0 and 1, respectively]. The location of the largest droplet was normalized by using the distance between the nearest and the farthest pinch-off droplets from the unperturbed interface.
4.2.6 Effect of particle size

A plot for the normalized tail diameter is shown in Figure 35 for Type 1 (36-55 µm) and Type 2 (67-91 µm) particles. These experiments were conducted for 50 wt% bitumen. The average residual tail diameter for 67-91 µm particles was larger than for 36-55 µm particles in the range of force ratios shown in Figure 35, but the scatter in the data disallowed us from commenting on the effect of particle size on the residual tail diameter/force ratio relationship. We also analyzed the median and the variation of the droplet sizes for the two particle sizes. The size and variance of droplet sizes for Type 2 particles was higher than Type 1 particles at similar force ratios [see Figure 36]. The origin of the variance in droplet sizes for Type 2 particles were traced to the satellite and sub-satellite droplets formed between primary droplets in the residual tail disintegration process as shown in Figure 37.

![Figure 35](image1.png)

Figure 35. A trend of normalized residual tail diameter with $\chi$ for 50 wt% bitumen for two different particle size range: Type 1(36-55 µm) and Type 2(67-91 µm).

![Figure 36](image2.png)

Figure 36. Droplet size distribution for Type 1 and Type 2 particles for pH 9.9 water and 50 wt% bitumen: (A) comparison of droplet size distribution for Outcome 2 (median and standard deviation) and the force ratio, and (B) the histogram of droplets formed in all Outcome 2 cases.
Figure 37. Satellite and primary droplets formed in Outcome 2. Particle penetration across 50 wt% bitumen and pH 9.9 process water interface, particle velocity = 223 mm/s, particle size = 105 µm × 77 µm (Satellite droplets are in red dotted circles).

### 4.2.7 Particle penetration time

The particle penetration time was defined in section 4.1.3. As will be explained later in section 4.2.9, it determines whether or not penetration will occur under industrial operating conditions. The penetration time ranged between a few milliseconds to a few hundred milliseconds, and was found to be inversely related to the force ratio and directly related to the viscosity of the oil phase as shown in Figure 38(A). The error in penetration time measurement was higher for 33 wt% and 50 wt% bitumen, because the number of frames that could be grabbed for the initial interaction at those viscosities were lower [see Figure 38(B)]. Unlike the model system (see Figure 23), a trend for normalized penetration time could not be established due to high variability in the data collected.

Figure 38. Trends for particle (A) penetration time, and (B) normalized penetration time at bitumen and process water interface (penetration time normalized using particle characteristic time scale)
4.2.8 Total emulsified water volume

The total emulsified volume relative to the particle volume for Type 1 (36-55 µm) particles is shown in Figure 39. The normalized emulsion volume was $O(10^{-3} - 10^{-2})$ for Outcome 1 and $O(10^{-2} - 10^{-1})$ for Outcome 2, suggesting that residual tail emulsification was responsible for the increased emulsification for 33, 50, and 67 wt% bitumen, and that it could be a very significant fraction of the particle volume. Overall, the normalized emulsion volume increased with the force ratio for 33, 50, and 67 wt% bitumen [see Figure 39 and 40].

The amount of fluid carried by a particle into the oil phase is governed by the balance between the entrainment rate and the drainage rate. The entrainment rate is the rate at which particle carries fluid into the oil phase and the drainage rate is the rate of drainage of the aqueous film between the particle and the interface. The increase in total emulsified volume upon increasing the force ratio at 33 to 67 wt% bitumen concentrations indicated that the entrained volume increased relatively more than the drained volume. Also, the same can be said for the larger normalized volume for 50 and 67 wt% bitumen at a pH of 9.9 and a constant force. But as with the breakup time, a detailed numerical study is required to understand the entrainment and drainage behavior for a surfactant-rich system.

![Figure 39. Total emulsified volume to particle volume ratio as a function of $\chi$ for Outcome 1 and Outcome 2 for Type 1 particles.](image)
4.2.9 **Particle Interaction with the bitumen-water interface in the extraction and froth treatment process:**

In the presented work, the force ratio, the normalized residual tail diameter, the normalized emulsified volume, and the droplet size distribution are the data sets critical for the oil sands industry. The volume of emulsification of bitumen via bitumen-water interaction with the particles can be estimated based on the collision frequency of the particles with bitumen-water interface, particle-interface interaction time-scale, flow conditions (e.g. average velocity, shear rate, energy dissipation rate, etc.) and fluid properties (e.g. density, viscosity, particle size, particle volume fraction). One way to locate susceptible zones in the extraction or froth treatment process is determine where particle concentrations are significant and the forces acting on particles are sufficiently large. Some zones where this criterion could be met are hydrotransport line, pumps to transport bitumen slurry ($\approx 30$-$35\%$ solids), pumps to transport bitumen froth ($\approx 10\%$ solids), bitumen froth-solvent mixing vessel, pumps to transport diluted froth to the inclined plate settlers, etc.

The results obtained from the microscale study showed that the force ratio for emulsification by particle penetration was minimum at 67 wt% bitumen. However, the viscous effects grew non-linearly from 67 wt% to 75 wt% bitumen and required higher force ratios for emulsification. The bitumen slurry has extremely low viscosity ratio (bitumen viscosity $O(1)$ Pa.s or more). Even though the bitumen slurry contains the largest particles, these particles might not be able to satisfy...
the conditions described in Section 4.2.9.1 to penetrate through the interface as the high viscous effects would require larger penetration times.

Once the bitumen froth is removed from the froth floatation unit, it is send to froth treatment section in the froth line. The bitumen froth is diluted using solvents to improve the separation efficiency of water removal from bitumen. The bitumen froth contains 10% solids and the average size of these solids is smaller than the one present in bitumen slurry. It was shown in this thesis that emulsification by the penetration of smaller particles lead to higher volume fraction of finer droplets. In the froth line and the solvent mixer chamber, the particle concentration might be intermediate to slurry and bitumen product concentration, however, the presence of smaller particle makes the formation of finer droplets more likely in this section. On top of particle concentration, the viscosity ratio is also in the range of the bitumen viscosity used in the microscale studies. Hence, the froth line and the solvent mixer unit have the largest probability of the formation of finer droplets.

### 4.2.9.1 Kolmogorov’s theory to calculate the minimum energy dissipation rate

We used Kolmogorov’s theory [46] to provide a quantitative measure of energy dissipation rate ($\dot{\varepsilon}$) range, wherein emulsification by the particle penetration across an interface can occur. There were two regimes relevant to this work: Kolmogorov scale and inertial subregime. The time scales and available force ratio was compared with the penetration time and $\chi$ value to find the limits within which emulsification via penetration could take place. The first condition required for a particle to penetrate across the interface is that the timescale of contact during a collision between the particle and the drop should exceed the penetration time reported in this thesis. Another requirement is that the available force ratio should be greater than the critical force ratios ($\chi_c$) measured in this thesis. For a particle to penetrate across an interface on an industrial scale, both the aforementioned conditions should be met. If both the particle and the drop are below the Kolmogorov scale, the conditions for particle penetration yield the following inequalities,

\[ t_p < \left( \frac{\nu}{\dot{\varepsilon}} \right)^{1/2} \quad (4.3) \]

\[ \chi = \frac{\mu (\nu / \dot{\varepsilon})^{1/2} d_p}{0.16 \gamma} > \chi_c \quad (4.4). \]

Based on (4.3) and (4.4), the energy
dissipation rate ($\dot{\varepsilon}$) is required to be in the following limits, $\nu \left( \frac{0.16 \chi_c \gamma}{\mu d_p} \right)^2 < \dot{\varepsilon} < \frac{\nu}{t_p^2}$ (4.5), which requires that $\frac{0.16 \chi_c \gamma t_p}{\mu d_p} < 1$ (4.6).

We found that for the penetration time reported in this thesis, the upper bound of energy dissipation rate ($\dot{\varepsilon}$) was in $10^{-3}$ to $10^1$ m$^2$/s$^3$ range for each bitumen concentration. However, the minimum force ratio ($\chi_c > 0.1$) condition likely not to be satisfied in Kolmogorov scale regime.

Let us now consider the case when both the particle and the drop are in the inertial sub-regime and the particle collides with the interface due to velocity fluctuations.

The conditions for particle penetration in inertial subrange yield the following inequalities:

$$t_p < \left( \frac{L^2}{\dot{\varepsilon}} \right)^{1/3} (4.7)$$

and

$$\chi = \frac{\rho (\dot{\varepsilon} L)^{2/3} d_p}{0.16 \gamma} > \chi_c \text{ (4.8).}$$

Based on these two inequalities, the energy dissipation rate must satisfy

$$\frac{1}{L} \left( \frac{0.16 \chi_c \gamma}{\rho d_p} \right)^{3/2} < \dot{\varepsilon} < \frac{L^2}{t_p^3} \text{ (4.9),}$$

which requires that

$$L > t_p \left( \frac{0.16 \chi_c \gamma}{\rho d_p} \right)^{1/2} \text{ (4.10).}$$

The following table provides the minimum dissipation rate and corresponding eddy length scale in inertial subrange for particle penetration.

<table>
<thead>
<tr>
<th>bitumen wt%</th>
<th>$d_p$ (µm)</th>
<th>$\rho$ (kg/m$^3$)</th>
<th>$\chi_c$</th>
<th>$t_p$ (ms)</th>
<th>$\gamma$ (mN/m)</th>
<th>$L$ (µm)</th>
<th>$\dot{\varepsilon}$ (m$^2$/s$^3$)</th>
</tr>
</thead>
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<tr>
<td>33</td>
<td>200</td>
<td>790</td>
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<td>1</td>
<td>10</td>
<td>32</td>
<td>1.01</td>
</tr>
<tr>
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<td>200</td>
<td>830</td>
<td>0.1</td>
<td>1</td>
<td>10</td>
<td>31</td>
<td>0.96</td>
</tr>
<tr>
<td>67</td>
<td>200</td>
<td>875</td>
<td>0.1</td>
<td>10</td>
<td>10</td>
<td>302</td>
<td>0.09</td>
</tr>
<tr>
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<td>20</td>
<td>790</td>
<td>0.1</td>
<td>1</td>
<td>10</td>
<td>101</td>
<td>10.13</td>
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<tr>
<td>50</td>
<td>20</td>
<td>830</td>
<td>0.1</td>
<td>10</td>
<td>10</td>
<td>98</td>
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<tr>
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<td>875</td>
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<td>10</td>
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<td>3024</td>
<td>0.01</td>
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</table>
4.2.9.2 Effect of particle size on minimum energy dissipation rate

The studies discussed in Section 2.2.3 suggested that the particle penetration time was related to characteristic time and/or capillary time scale. These studies were conducted for particle penetration under the influence of gravitational force. However, the particle penetration studies in this thesis were conducted using magnetic force. Therefore, the characteristic time scale and capillary time scale were compared to find out which would be dominant. The ratio of capillary time scale to characteristic time can be given as \[ \frac{\mu d_p / \gamma}{d_p / v} = Ca \]. This time scale ratio shows that at lower force ratio, Ca \sim O(1) or less, characteristic time scale dominates the penetration time, whereas, at Ca > 1 i.e. \( \chi > 6.25 \), the capillary time scale dominates the penetration time.

Here, we discuss how the particle size would affect the particle penetration on industrial scale. This scaling analysis is valid for a surfactant-free interface and care should be taken when using the analysis for a surfactant-rich system. It could be possible that when a particle impinges on the interface, the surfactant composition of the interface changes with the particle size, which would eventually change the interfacial properties. Therefore, a detailed numerical study would be required before commenting on the applicability of the analysis for a surfactant-rich system.

Regardless of the particle size \( \chi > \chi_c \) i.e. for the same fluid and interface properties at equal force ratio, \( v_1^2 d_{p1} = v_2^2 d_{p2} \) (4.11). This formula clearly indicates that smaller particles are required to have larger velocities to overcome the minimum force ratio \( \chi_c \).

When the particle penetration time is related to the characteristic time scale \((v / d_p)\) then

\[ \frac{t_{p1}}{d_{p1} / v_1} = \frac{t_{p2}}{d_{p2} / v_2} \] (4.12).

(4.11) and (4.12) can be combined to deduce the dependence of the penetration time on the particle diameter as

\[ \frac{t_{p1}}{t_{p2}} = \left( \frac{d_{p1}}{d_{p2}} \right)^{1/2} \] (4.13).

For the same fluid and interface properties, the length scale of eddies in inertial subrange can be deduced as

\[ \frac{L_1}{L_2} = 1 \] (4.14).

In inertial subrange, the energy dissipation rate \( \dot{\varepsilon} \) is equal to \[ \frac{L^2}{t_p^3} \] (4.13) and (4.14) can be combined to relate the minimum energy dissipation rate with particle
size as \( \frac{\dot{\varepsilon}_1}{\dot{\varepsilon}_2} = \left( \frac{d_{p2}}{d_{p1}} \right)^{3/2} \) (4.15), given particle penetration time was related to characteristic time scale.

When particle penetration time is related to the tail breakup time scale, then \( \frac{t_{p1}}{d_{p1}} = \frac{t_{p2}}{d_{p2}} \) (4.16).

For the same fluid and interface properties, the length scale of eddied in inertial subrange can be deduced as \( \frac{L_1}{L_2} = \left( \frac{d_{p1}}{d_{p2}} \right)^{1/2} \) (4.17). On combining (4.14) and (4.15), the minimum dissipation energy can be related with particle size as \( \frac{\dot{\varepsilon}_1}{\dot{\varepsilon}_2} = \left( \frac{d_{p2}}{d_{p1}} \right)^2 \) (4.18). Overall, for the same fluid and interface properties, the minimum dissipation rate (\( \dot{\varepsilon} \)) can be related to particle size as \( \dot{\varepsilon} \propto \frac{1}{d_p^\alpha} \), where \( 1.5 < \alpha < 2 \), i.e. larger dissipation rates are required to penetrate smaller particles through the interface.
5.1 Conclusions

An experimental microscale study of ferromagnetic iron particle penetration across surfactant-free (mineral oil and aqueous-organic mixture) interface and surfactant-rich (bitumen-water) interface not only visually demonstrated the formation of extremely fine droplets as small as 1.9 µm in the oil phase, but also elucidated the emulsification mechanisms. Surfactant-free experiments were conducted for [light mineral oil (LMO) or heavy mineral oil(HMO)] and [water and IPA in 1:2 (AQ1) or 2:1 (AQ2) volumetric ratio] interfaces, whereas, surfactant-rich experiments were conducted for (33, 50, 67, or 75) wt% bitumen and pH (8.3 or 9.9) of process water. The smallest emulsified droplets produced were about 1.9 µm and smaller droplets could have formed, however, we were limited by the optical resolution. When a particle with a constant force impinged onto the interface, it either stayed at the interface or penetrated through the interface beyond a critical force ratio ($\chi$). Once a particle penetrated through the interface, it did not form any observable droplets (Outcome 0 – no emulsification) for smaller force ratios, but for larger $\chi$, particle penetration led to the formation of droplets. The emulsification occurred via two mechanisms – pinch-off emulsification (Outcome 1) and residual tail emulsification. The residual tail emulsification was always preceded by pinch-off emulsification, and therefore, we defined Outcome 2 as pinch-off and residual tail emulsification. The data revealed that $\chi$ (no penetration) < $\chi$ (Outcome 0) < $\chi$ (Outcome 1) < $\chi$ (Outcome 2).

LMO and (AQ1 or AQ2) system were dynamically similar and the force ratio for the transition from Outcome 0 to 1 occurred at 0.2. The $\chi$ values for Outcome 0-1 and 1-2 transitions were higher for lower viscosity ratio due to relatively higher drainage rate. The relatively higher drainage rates for lower viscosity ratio resulted in the lower entrained volume at the same $\chi$ values for the surfactant-free system. However, the critical force ratios for 0-1 and 1-2 transitions for the bitumen-water system was lower than the surfactant-free system. Also, the various bitumen-water systems explored in this work were found not to be dynamically similar. The $\chi$ values for 0-1 and 1-2 transitions for 67% bitumen and a process water of pH 9.9 were approximately 0.05 and 0.2, respectively. When compared to clean interfaces, penetration across the water-bitumen interface occurred at the force ratios that were an order of magnitude smaller. This was attributed to the difference in the dynamic and equilibrium interfacial tensions of the water-bitumen interface.
The normalized residual tail diameter was between 0.02 – 0.04 for the values of $\chi$ corresponding to the beginning of the residual tail emulsification regime for the bitumen-water system. This suggested that if a particle of size 50 µm impinged on the interface and formed a residual tail, its diameter could be as small as 1 to 2 µm.

The residual tail emulsification for the bitumen-water system was reminiscent of surfactant-mediated tip-streaming, however, it was absent in the surfactant-free system. Surfactant-mediated tip-streaming was responsible for the formation of fine water droplets at lower force ratios, whereas, the satellite droplets were accountable for the presence of fine water droplets at higher force ratios. The formation of satellite droplets increased the standard deviation of droplet size distribution at higher $\chi$. The droplet size distribution had higher variance for Type 2 (67-91µm) particle size in comparison with Type 1 (36-55µm) due to the formation of satellite droplets with primary droplets. It is noteworthy that irrespective of the force ratio, particle size, bitumen concentration and process water pH, droplets of size 2-3 µm were observed for residual tail emulsification. The fractional volume of larger droplets and the total normalized emulsified volume was higher at higher force ratios. The emulsified volume was found to be as much as 10% of the particle volume for a single particle penetration event at $\chi > 1$, particularly at a pH 9.9 of process water.

The penetration time was a few milliseconds to a few hundred milliseconds for the bitumen-water system. The analysis of energy dissipation rate using Kolmogorov’s theory by comparing penetration time with the time scale of eddies showed that the particle penetration across the interface could occur on the industrial scale in inertial subrange. For a surfactant-free system, the scaling analysis showed that the minimum energy dissipation rate was inversely proportional to $d_p^\alpha$, where $1.5 < \alpha < 2$, i.e. smaller particles would require larger minimum energy dissipation rate to penetrate through the interface.

Finally, a qualitative analysis suggested that the highest likelihood of the formation of these fine droplets is in the froth line and in bitumen dilution unit. A scaling analysis revealed that the eddies in the inertial subrange can lead to energy dissipation rates that can cause particle penetration.
5.2 Future work

In this work, we were restricted by the experimental requirements to conduct the particle penetration in a certain force range and that required us to use ferromagnetic particles. The irregular shapes and sizes of these particles probably contributed most strongly to the variability and error in the collected data. One approach to reduce the variability could be to use spherical ferromagnetic microparticles generated, for example, via a microfluidic emulsification method [48]. A second way of improving the experimental data is to use a trigger-based particle impinging mechanism. In our experiments, we simulated this trigger by manually moving the magnet towards the device with an impulse. But the majority of particle penetration events occurred during the movement of the magnet. This limitation constrained us to deduce the force on the particle by examining the particle trajectory, which led to errors in the calculated drag forces. If the trigger were based on an electromagnet, for example, it would have been possible to deduce the force acting on the particle from a numerical calculation based on the strength of the magnetic field, the magnetic susceptibilities of the particle, and the surrounding media.

The absence of a fast trigger also prevented us from recording videos at frame rates exceeding 2000 fps, as time was lost in manually bringing the magnet closer to the interface. If a suitably fast trigger such as an electromagnet were employed, particle penetration events up to the highest recording speed of the camera (750,000 fps) could be captured. This would significantly reduce the error in penetration time measurement and allow us to observe the pinch-off emulsification for lower bitumen concentration.

Ensuring the constancy of particle size and magnetic force would make the experiments reproducible. This would permit us to take videos that alternated between a field of view that captured the emulsification phenomena in the bitumen phase, to a field of view focused on the region upstream of the interface that would allow us to calculate the particle velocity as it impinged the interface.

Apart from the modification proposed in the experimental setup, a detailed numerical study of particle penetration could improve our fundamental understanding of the phenomenon, and especially, the water droplet formation. Numerical studies of particle impingement at the interface have been conducted in the past to report tail diameter and aqueous phase film thickness. However, these simulations are terminated when the tail becomes very thin at the pinch-off location because
higher computation power is required. A modification to these numerical schemes is needed to continue these simulations beyond pinch off and breakup. Also, the mathematical model should also incorporate adsorption-desorption kinetics of surfactants at the interface and the effect of surfactants on interfacial properties, both of which, according to our work, are key for capturing the dynamics of drainage, tail formation, and capillary instability accurately.
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