

Determining frother-like properties of process water in bitumen flotation



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ABSTRACT

In oil sands flotation, bitumen is known to release natural surfactants into the process water following the addition of NaOH. These surfactants appear to replace the need for frother. Measuring the Sauter mean diameter (D_{32}) vs. dilution, it was possible to characterize the frother-like properties of process waters as an equivalent concentration of a known frother commonly used in mineral flotation, DF-250. Process water samples from the thickener overflow at the Shell Albion plant were examined. The study showed equivalent concentrations up to 60 ppm DF-250 and variations between samples. Reasons for the variability are discussed. A gas holdup vs. D_{32} correlation was established which reduced the experimental effort.

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1. Introduction

The oil sands of Canada are among the largest reserves of hydrocarbons in the world, containing the equivalent of 1.7 trillion barrels of oil, of which 170 billion barrels are recoverable using current technology (ERCB, 2011). The oil sands are found as unconsolidated sandstone deposits consisting of very heavy crude (bitumen) and sand, separated by a thin film of water containing mineral rich clays (Clark, 1944; Takamura, 1982; Czarnecki et al., 2005). The largest deposits are found in the Athabasca region in Alberta, with the Wabiskaw–McMurray deposit containing the highest bitumen concentrations. All large open-pit mining operations such as Albion Sands (Shell), Syncrude, Suncor, Horizon (CNRL) and Kearl (Imperial Oil) are located in this area, with bitumen ore grade ranging from 9 to 13 wt.% and a total established mineable bitumen reserve of 27 billion barrels (ERCB, 2011; Masliyah et al., 2011).

The current method of extracting bitumen from the oil sands is the Clark hot-water extraction process. In this process, the mined oil sands are conditioned with caustic soda (NaOH) and hot water (50–80 °C), aerated and transferred using pipeline hydrotransport to a large gravity separation tank (the primary separation cell, or PSC) (Clark, 1929; Clark and Pasternak, 1932; Masliyah et al., 1981, 2011; Schramm, 2000). Most of the bitumen is recovered in a rich froth formed in the PSC. A middlings stream drawn from the central part of the PSC, and tailings drawn from near the

bottom of the PSC are sent to conventional mechanical flotation cells to recover the remaining bitumen. The process has been shown to produce high recoveries for bitumen-rich estuarine ores, although poorer performance on leaner marine ores (Schramm and Smith, 1985a).

A key characteristic of the Canadian oil sands is the thin water film surrounding the sand grains, which renders them easy to release from the bitumen using water-based methods such as the Clark hot-water process. The extraction process decreases the viscosity due to the temperature increase and releases natural surfactants from the bitumen due to the addition of caustic and increase in pH (Leja and Bowman, 1968; Sanford, 1983). The combination facilitates ablation of bitumen-sand lumps and release (liberation) of bitumen from the sand using mechanical agitation (Takamura and Chow, 1985; Schramm and Smith, 1985a; Hupka and Miller, 1991). Depending on the ore grade and the amount of fine particles, different levels of NaOH are needed to release sufficient surfactants to reach what is termed the critical free surfactant concentration, the concentration which maximises bitumen recovery (Schramm and Smith, 1985b, 1990a, 1990b). Rich ores require less caustic to reach the critical surfactant concentration than lean ores.

The surfactants released following caustic addition are predominantly aliphatic carboxylates – $\text{CH}_3(\text{CH}_2)_{x-4}\text{COONa}$ – with carbon chains ranging from C_{15} to C_{17} (Schramm and Smith, 1987; Schramm, 2000). Tailings and recycled water are also shown to be rich in a mixture of carboxylic acids known as naphthenic acids and their water-soluble and surface active sodium salts (Mackinnon and Boerger, 1986; Holowenko et al., 2000). The concentration of

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naphthenic acids in the process waters was found to be in the range of 30–125 mg/L (Schramm, 2000; Holowenko et al., 2000) of which approximately 2% are water soluble salts (Masliyah et al., 2004). Direct addition of surfactants in-lieu of NaOH was explored and shown to deliver good recovery without the need for high pH levels (Sanford, 1981).

One factor that may enhance flotation is the impact of the released surfactants on reducing bubble size. In mineral flotation systems reduction in bubble size is commonly achieved with frother. Frothers reduce bubble size (diameter) from typically 4–5 mm in water only, to 1 mm or less (Nesset et al., 2006) which can increase flotation kinetics by a factor of 10 or more (Ahmed and Jameson, 1985). Frothers adsorb at the air/water interface (Leja and Schulman, 1954) and are commonly held to aid reduction in bubble size through coalescence prevention (Harris, 1976). The surfactants released in bitumen processing may also adsorb at the air/water interface and act in similar manner to frothers, to reduce coalescence and promote bubble size reduction.

A method to characterize the bubble size reduction function of frothers is to plot the Sauter mean bubble diameter (D_{32}) against frother concentration (C). The D_{32} represents the mean size of a bubble having the same total bubble volume to surface area ratio as the bubble size distribution. Given that flotation is driven by bubble surface area, the D_{32} is the mean size often used in flotation studies. To determine bubble size distribution and calculate D_{32} , various devices are available (Tucker et al., 1994; Grau and Heiskanen, 2002; Rodrigues and Rubio, 2003) including the McGill Bubble Size Analyzer (MBSA) (Hernandez-Aguilar et al., 2004; Gomez and Finch, 2007).

The D_{32} - C plot shows an initial rapid decrease in D_{32} as frother concentration is increased but levels off to become approximately constant beyond a particular frother concentration, which could represent the concentration at which all bubble coalescence is prevented. Cho and Laskowski (2002) defined this concentration as the 'critical coalescence concentration' (CCC) thus introducing a parameter to compare different frothers with respect to their effect on bubble size reduction. A recent publication details the CCC for a range of frothers (Zhang et al., 2012). Laskowski (2003) used a graphical method to estimate CCC. The work presented here fitted the D_{32} - C data to a three-parameter exponential decay model to determine the CCC-95, i.e., the concentration giving 95% of the bubble size reduction compared to water alone. The CCC-95 was shown to closely approximate the CCC values determined graphically (Nesset et al., 2007; Finch et al., 2008; Zhang et al., 2012).

Gas holdup (E_g) has recently been proposed as an alternative to bubble size for characterizing frothers (Azgomi et al., 2007). Gas holdup is the volume of gas relative to the volume of the gas-liquid (slurry) mix. As bubble size reduces, gas holdup increases since small bubbles rise slower than large bubbles (Clift et al., 1978). This means gas holdup may substitute for bubble size, the advantage being that gas holdup is easier to measure than D_{32} . Bubble size and gas holdup are referred to as 'hydrodynamic' characteristics that are analyzed using various gas dispersion instruments that have helped improve frother selection and distribution strategies (Cappuccitti and Nesset, 2009).

Few studies on hydrodynamics in bitumen flotation have been conducted. Small bubbles are claimed to lead to better bitumen-bubble attachment due to shorter induction time and are considered beneficial for bitumen flotation (Yoon and Luttrell, 1989; Gu et al., 2004). Zhou et al. (2000) studied the effect of process water chemistry on gas dispersion in bitumen flotation by measuring the gas holdup in a water column and inferring bubble size using drift-flux analysis. They showed that gas holdup increased (bubble size decreased) with an increase in NaOH concentration. They also highlighted the relationship between smaller bubble size and higher bitumen recovery. Direct measurement of bubble size in

flotation cells treating bitumen reported small bubbles (ca. 1 mm) (Gomez, 2007), which reasonably could be attributed to the released surfactants. A way to characterize the impact of the released surfactants on the hydrodynamics is required.

It is not feasible to isolate the individual surfactants responsible for bubble size reduction to determine the CCC by the conventional method of adding known concentrations and measuring D_{32} , for discussion purposes referred to as the 'addition' method. Instead, treating the system as a whole, Nassif et al. (2013) proposed a 'dilution' method, measurement of D_{32} vs. dilution volume and, by comparison with the D_{32} - C for a known frother, translate the dilution values to frother equivalent concentrations. They also explored the use of gas holdup as a substitute for bubble size measurement. The frother concentration equivalence gives the 'frother potential' ('hydrodynamic potential') of process water in readily understood terms. The purpose of this paper is to use the dilution method to determine the hydrodynamic potential of process waters sampled from the Albian Sands plant.

2. Apparatus and methodology

The experimental set-up, a 7.6 cm diameter, 3 m high column (Fig. 1), was assembled at Coanda's research facility in Edmonton using specifically designed scaffolding. A cylindrical porous stainless steel sparger mounted vertically at the bottom of the column (10 μ m nominal porosity) dispersed air into bubbles at a set gas rate of 2.14 L/min or gas superficial velocity (J_g) of ca. 0.7 cm/s (at the sparger). The set-up was operated in closed loop with the overflow returning to the mixing tank and pumped back to the bottom of the column co-current to the air flow. The feed was introduced into the column using a peristaltic pump (Cole Palmer Model 7520-25) at a constant 3.4 L/min. The conditions ensured that no significant froth layer formed during the experiments (a froth layer is not desirable as it removes some of the surfactants from the water and can interfere with the upper pressure tapping point).

Gas holdup was calculated from differential pressure (ΔP) measured using Bailey model PTSDDD1221B2100 tapped between 170 cm and 260 cm from the base as follows:

$$E_g = \frac{\Delta P}{L} * 100 \quad (1)$$

where ΔP is in cm of water and L is the distance (cm) between the tapping points. Absolute pressure P_{abs} (No-Shok pressure sensor) at the base of the column was recorded to check level. Air flow was controlled using a calibrated flow meter. All instruments were connected to an interface and portable signal conditioner, which in turn relayed and recorded the data on an Intellution iFix platform installed on a laptop.

Bubble size distribution was measured using the MBSA comprising a 6 L, PVC viewing chamber with opposing sloped (15°) windows made of reinforced glass connected to a sampling tube which is inserted into the column to collect bubbles. Facing the upper window is a high resolution camera (Canon 60D with macro lens) with backlighting to create bubble shadow images.

The procedure for bubble size determination is described in detail elsewhere (Nassif et al., 2013). DF-250 was selected for the known frother to validate the dilution method. The process water samples were received from Muskeg River Mine (MRM) extraction facility at Shell Albian Sands in sealed 20 L pails. They were collected from the thickener overflow (OF), with one sample from the recycle water stream (RCW). The thickener OF sampling point was chosen considering its proximity to the flotation section (it is the hydrodynamics in flotation that is the interest) whilst having minimal bitumen content. The waters were allowed to settle for

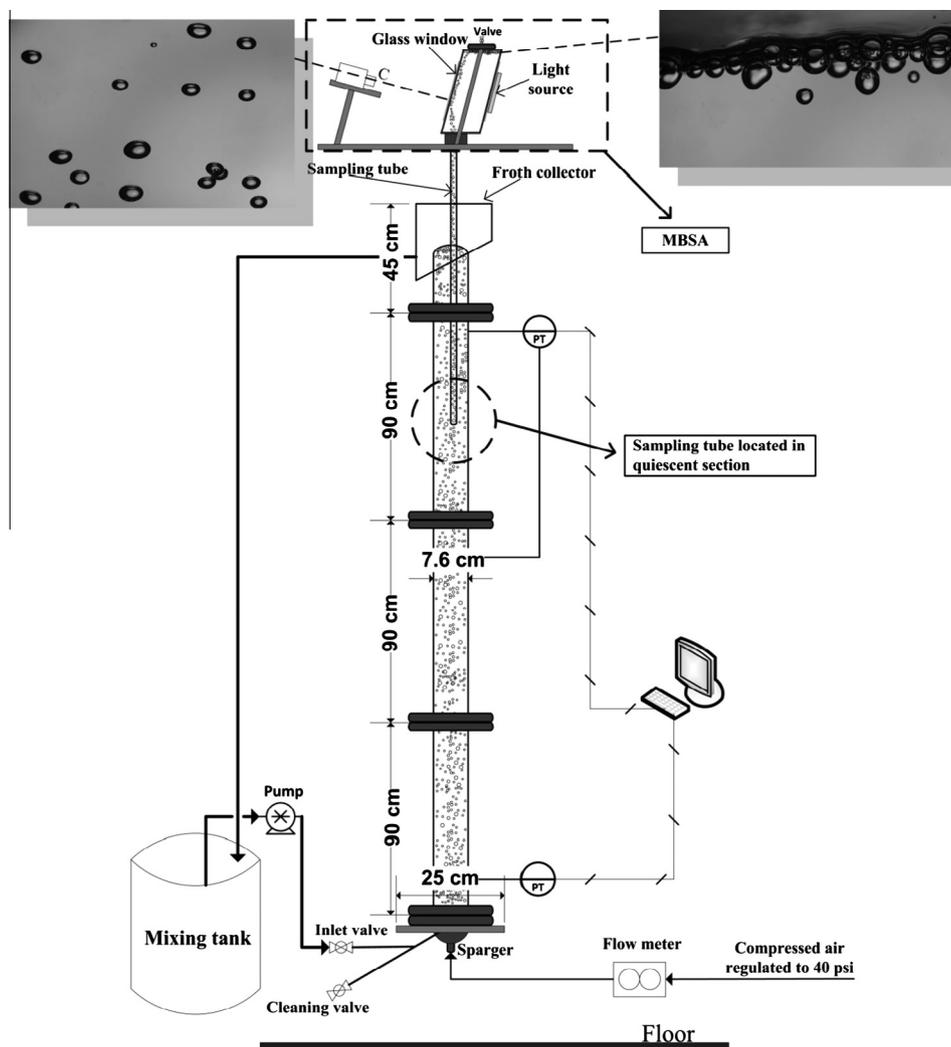


Fig. 1. Column set-up with McGill Bubble Size Analyzer (MBSA).

at least a week prior to opening the seal such that any clay and silt settled at the bottom of the pail and any bitumen aggregated at the top. This allowed essentially clear water to be pumped out from the mid-section of the pail. Clear water facilitates use of the MBSA and avoids clogging the porous sparger. For dilution Edmonton tap water was used (composition found online: Epcor 2012)¹. The dilution water was added with the air flow turned off intermittently to allow adequate mixing as judged by steady gas holdup readings. The water temperature ranged between 12 °C and 14 °C. Fig. 2 shows the current flow sheet of the Muskeg River Processing Plant, detailing the position of the thickener in the process.

3. Results

3.1. DF-250 CCC curves

The DF-250 addition and dilution test results in Fig. 3 show excellent agreement, similar to previous work (Nassif et al., 2013). Fitting to the decay model was by the least squares method (Microsoft Excel 2010 Solver). The critical coalescence concentration was determined based on the three-parameter model (CCC-95).

3.2. Process water dilution curves and DF-250 frother equivalence

Keeping the operating parameters consistent with the DF-250 tests (liquid flow rate and gas velocity), dilution curves were developed for the process water samples (Fig. 4). The concentration scale in these tests is the ratio of the remaining volume of original process water to the total volume of the diluted solution. Samples collected on September 30th and October 1st were tested the week of October 18th. The rest of the samples were tested 3 weeks later over a span of 2 weeks. The DF-250 concentration data were converted to volume percent (%v/v) and included in Fig. 4 (upper scale) in order to determine DF-250 equivalent concentrations.

Fig. 4 shows that the dilution curves of process water samples exhibit a similar trend to that of DF-250. Using the procedure described in Nassif et al. (2013) where DF-250 equivalence is determined by equating the D_{32} values, the 5 thickener OF samples all have an undiluted equivalent concentration of ca. 60 ppm DF-250 and the RCW an equivalent concentration of ca. 24 ppm DF-250.

The images in Fig. 5 demonstrate the similarity in bubble size between undiluted process water samples and equivalent DF-250 concentration. (The RCW sample is compared to 20 ppm DF-250 instead of 24 ppm as the closest available set of images). Note the slightly darker background in the thickener overflow sample image due to higher turbidity caused by suspended solids, believed to be clays.

¹ <http://www.epcor.com/water/reports-edmonton/Documents/wq-edmonton-quality-assurance-2012.pdf>

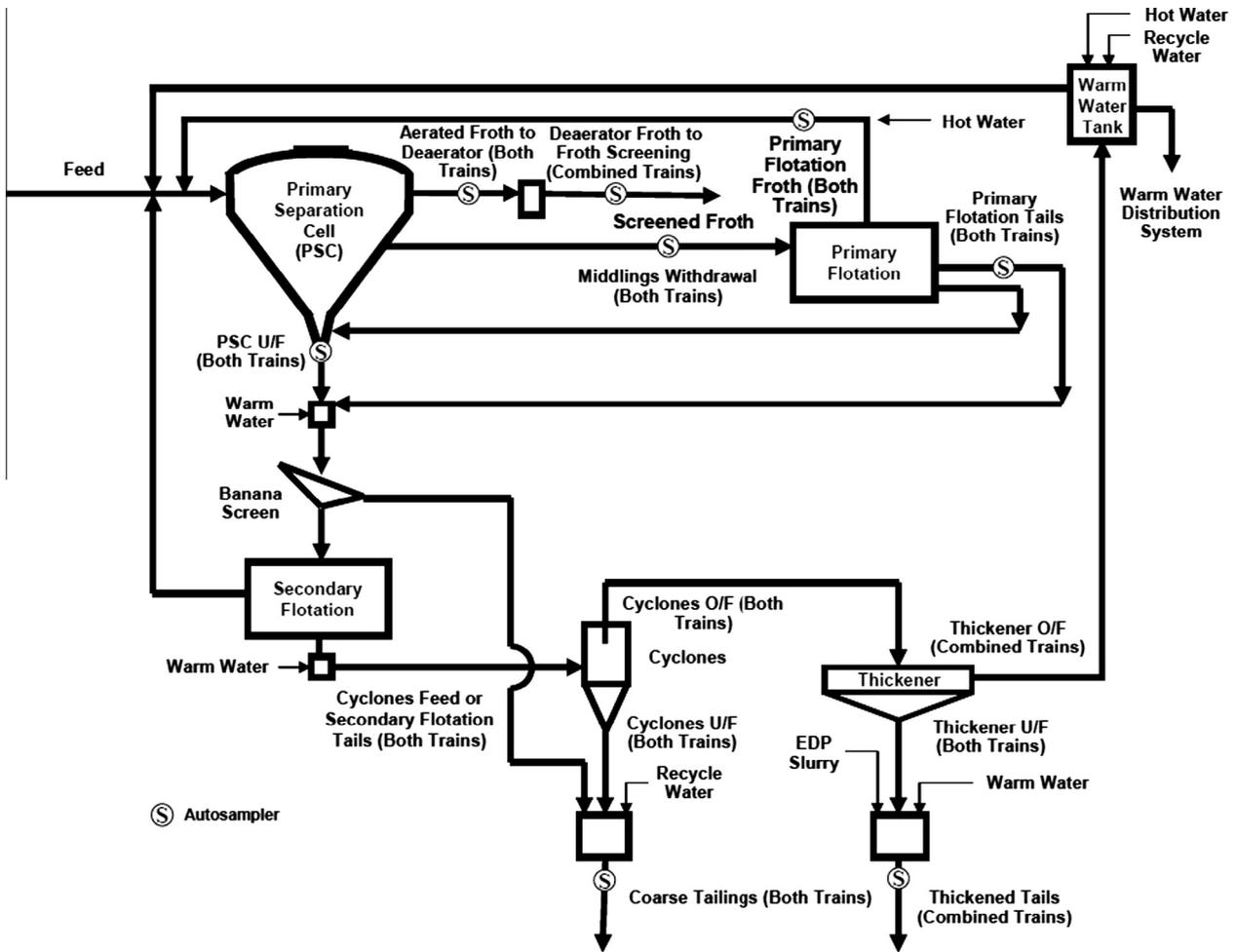


Fig. 2. Flow sheet of the Muskeg River Mine processing plant (Shell Canada Ltd., 2005).

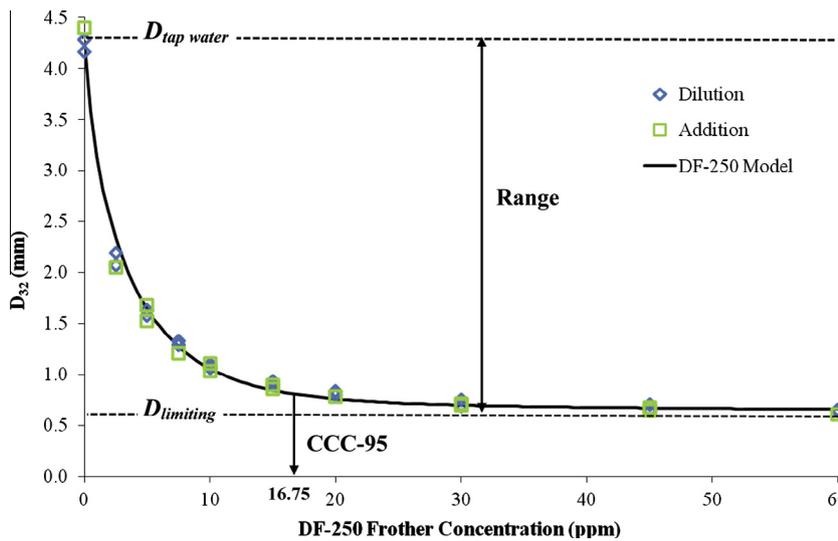


Fig. 3. Sauter mean bubble diameter D_{32} as a function of concentration for addition and dilution tests using DF-250.

The process water samples show variability in the Sauter mean diameter (D_{32}) with dilution summarized by their CCC-95%v/v values (Table 1). To convert the CCC-95%v/v to DF-250 equivalent concentrations requires a modification of the procedure. In the original procedure, equivalence is determined by

equating D_{32} values but at the CCC-95 the D_{32} is essentially the same and thus differences in the DF-250 equivalent concentration are lost. In the modification, comparisons were made on the basis of equivalent dilutions. To illustrate, the estimated CCC-95 for thickener OF September 30, 32% v/v, is equivalent to ca. 19 ppm

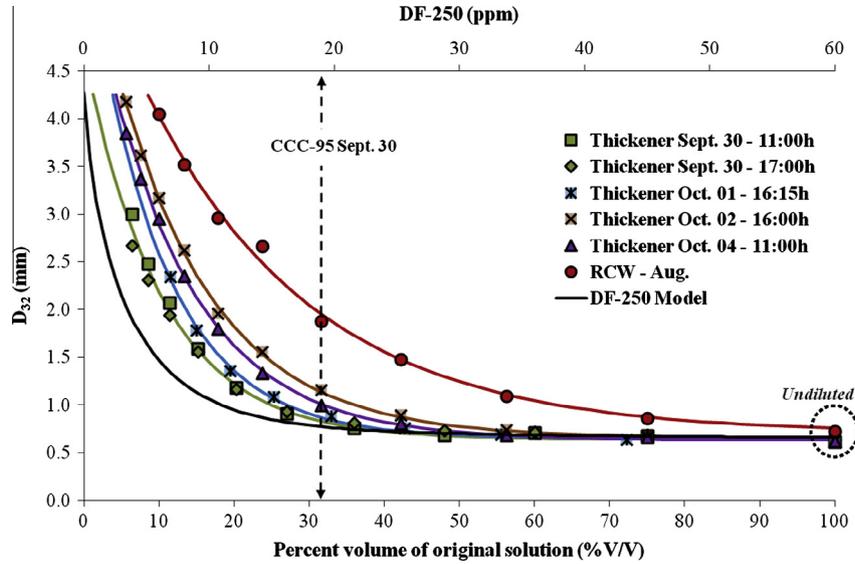


Fig. 4. Sauter mean diameter (D_{32}) as a function of process water concentration by volume for the Albian Sands process water samples.

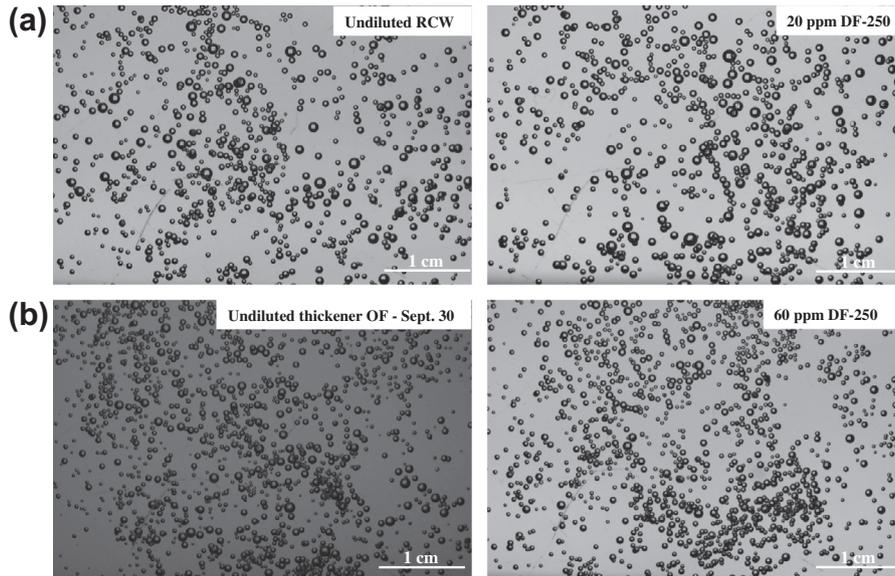


Fig. 5. Comparison of bubble size between process water samples (left) and water/DF-250 samples (right): (a) undiluted RCW and 20 ppm DF-250 and (b) undiluted thickener sample September 30 and 60 ppm DF-250.

DF-250. Using the same procedure, Table 1 is completed for the remaining samples.

3.3. Substituting gas holdup for bubble size

As the concentration decreases with dilution, bubble size increases with a corresponding increase in rise velocity and decrease in gas holdup; this trend is seen in Fig. 6 which shows D_{32} as a function of gas holdup (E_g) constructed from the process water data (all samples). The model was developed based on a logarithmic relationship (Eq. (2)):

$$D_{32} = -\tau \cdot \ln \left(\frac{E_g - E_{g,min}}{E_{g,max} - E_{g,min}} \right) \quad (2)$$

where τ is a constant, $E_{g,min}$ is minimum gas holdup, $E_{g,max}$ is maximum gas holdup. Optimal values for the constant, minimum holdup and maximum holdup were determined using least squares

Table 1
Summary of results for CCC-95 quoted in %v/v and in DF-250 equivalence (ppm).

Sample	CCC-95 (%v/v)	CCC-95 (DF-250 equivalence, ppm)
Thickener September 30	32	19
Thickener October 01	34	20
Thickener October 02	45	27
Thickener October 04	41	25
RCW – August	75	45

method (Microsoft Excel 2010 Solver). The values were 0.62 mm, 3.7% and 28.1% respectively.

The DF-250 data were included in Fig. 6 and essentially show the frother has the same bubble size control ability as the process waters as the data mostly fall within the 95% prediction limit of the model. (Data with Sauter mean diameter larger than 2.5 mm were

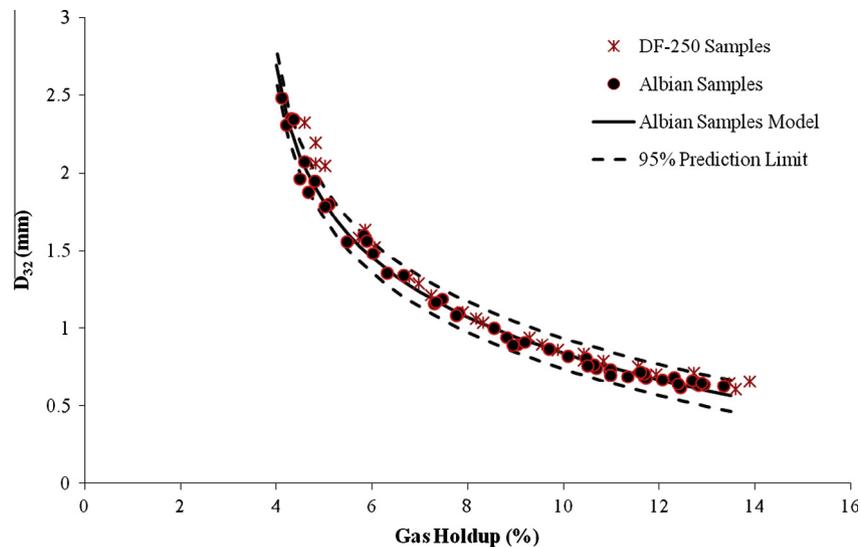


Fig. 6. Sauter mean bubble diameter D_{32} as a function of gas holdup: correlation model based on Albian samples data.

excluded as they do not lie within the region of interest and also exhibit high variation because of the steepness of this part of the curve). Fig. 6 shows that D_{32} can be approximated from E_g , a procedure taking less than 5 min compared to more than an hour using the MBSA (including image analysis).

4. Discussion

The addition of NaOH and the resulting surfactants released in processing bitumen ore, in addition to the ionic and clay components, lead to a complex and variable water chemistry that affects bitumen recovery (Schramm and Smith, 1987; Kasongo et al., 2000; Ding et al., 2006; Zhao et al., 2009). It is recognized that when evaluating flotation systems it is important to allow for water chemistry effects (Klimpel and Hansen, 1987; Crozier and Klimpel, 1989; Klimpel and Isherwood, 1991; Comley et al., 2002). The aim of the current work was to analyze the impact of Albian Sands water chemistry on the system hydrodynamics by measuring two gas dispersion parameters, bubble Sauter mean diameter and gas holdup. While other factors may have some role, the released surfactants likely contribute most of the hydrodynamic properties and thus it was logical to apply the bubble size and gas holdup techniques developed to characterize frothers.

Using the methodology introduced by Nassif et al. (2013) the system hydrodynamics were expressed in terms of DF-250 equivalent concentration. Estimates of the equivalent DF-250 concentration for the undiluted in the case of the thickener overflow gave ca. 60 ppm DF-250 equivalent. The dilution curves showed different CCC-95 values between the samples. The differences might suggest different surfactant types or combinations, but because CCC-95 is quoted as %v/v rather than absolute concentration, there may be an effect of initial undiluted concentration. For example, the RCW CCC-95 in DF-250 equivalence is 45 ppm but this water may have the same surfactant composition as the thickener OF but is more dilute. Nevertheless, the surfactants appear to be weaker than DF-250 as their CCC-95 values are higher than that of DF-250 (ca. 10–12 ppm).

Another point that appears to be related to the use of dilution ratio instead of concentration is the fact that the curves do not converge to the same D_{32} with increasing dilution. The converging value D_{32} should be that of tap water.

Variations in surfactant composition and concentration are believed to be related to the bitumen content of the ore. Variations in

surfactant release could result in varying hydrodynamic conditions making flotation difficult to control. In the present case, certainly the undiluted thickener OF samples appear to have DF-250 equivalents capable of supporting the hydrodynamic conditions necessary for flotation.

A change in composition of bitumen process waters has been shown to result from the biodegradation of water-soluble naphthenic salts by naturally occurring bacteria (Herman et al., 1994; Holowenko et al., 2001). Biodegradation is encouraged when process water is isolated from bitumen over an extended period of time such as in the tailings pond, or a possibility in the case of this work, storage of the water samples. Another important degradation process is precipitation of these anionic surfactants at low pH and in the presence of calcium and/or magnesium ions (Masliyah et al., 2011). These degradation processes may contribute to the variation in the process waters especially between thickener samples and RCW.

In the previous paper (Nassif et al., 2013), process water samples from the thickener OF had been aged for months following transportation to and storage at McGill, and when tested showed undiluted 20 ppm DF-250 equivalence. This represents a 67% decrease in frother potential compared to the current thickener OF samples that is difficult to attribute solely to a change in bitumen ore quality: ageing effects are suspected. One consequence is the need to test samples soon after collection. This is the reason the set-up was established at Edmonton to be nearer to the source. Ideally testing should be at the plant.

Compared to bubble size, gas holdup is more readily measured in the two-phase system. Gas holdup was modelled against D_{32} (Fig. 6) which facilitated estimation of D_{32} which greatly speeded up the assessment of the process waters. Fig. 6 shows the D_{32} – E_g trend for DF-250 agrees with that for the process samples, which further supports the use of DF-250 as the appropriate frother for determining the equivalence in this case.

The water samples supplied were ones readily available and low in bitumen. The thickener overflow samples represent conditions close to those in the flotation circuit but ideally we should include samples directly from the process units. One sample from the PSC middlings stream was taken and clarified water extracted after a period of settling. Although there was not sufficient volume to test undiluted, a 67% diluted sample gave a gas holdup of 12.6% with estimated D_{32} (from Fig. 6) of 0.62 mm. Since this dilution-gas holdup data fitted the trend for the current samples it suggests the original (undiluted) PSC water was at least comparable in

frother potential to the undiluted thickener overflow. The use of gas holdup combined with knowledge of the dilution-gas holdup trend opens a quick way to check other process unit waters for frother potential.

The next stage is to transfer the characterization techniques to site such that a range of fresh samples from various sampling points can be tested over time. One objective would be to establish variability in process water hydrodynamics and link with operating conditions, for example bitumen grade and fines content. There may be a case for addition of a frother to smooth out variations in the hydrodynamics. Variability in water quality will most likely increase as a consequence of leaner ores being treated, and as new methods are being developed to decrease the process temperature and to enhance recycle of tailings water (Sanford, 1981; Schramm et al., 2002; Masliyah et al., 2011). Another ambition is to consider using gas holdup for on-line monitoring of process waters hydrodynamic potential.

5. Conclusions

This paper describes a dilution method used to express the hydrodynamic potential of bitumen process waters as a DF-250 frother equivalent concentration. The method uncovered the high DF-250 equivalence (ca. 60 ppm) of thickener overflow process waters and identified variability between water samples that may be related to characteristics of the released surfactants. The use of gas holdup in place of bubble size determination greatly speeded up the measurement.

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