Rate of Bitumen Film Transfer from a Quartz Surface to an Air Bubble as Observed by Optical Microscopy

Dariusz Lelinski¹, Jaroslaw Drelich², Jan D. Miller³* and Jan Hupka⁴

¹ FFE Minerals USA Inc. Salt Lake City, UT 84106, USA
² Department of Materials Science and Engineering, Michigan Technological University, Houghton, MI 49931, USA
³ Department of Metallurgical Engineering, University of Utah, Salt Lake City, UT 84112, USA
⁴ Department of Chemical Technology, Gdansk University of Technology, 80-952 Gdansk, Poland

Oils from natural deposits and those produced by the petroleum industry have a very broad range of physico-chemical properties. Viscosity, density, interfacial tension, and surface charge are among the properties which usually have an influence on the selection of an oil recovery technology and the selection of appropriate operating conditions. For example, the density of many oils is similar to the density of water, and their separation from the aqueous phase cannot be realized in a gravitational force field. In such cases, oils must be “filled” with a volume of gas, light solvent, or light solid particles to make them less dense than the processing water. One of the filling procedures is flotation, gas intrusion into the oil phase, a most popular separation technique used in oil recovery from aqueous suspensions.

Froth flotation is a common separation process for the recovery of oil from oil sands (Miller and Misra, 1982; Oblad et al., 1987) and contaminated soil (Anderson, 1993; Friend, 1996). In the froth flotation technique, two major separation steps must be accomplished: i) oil release from mineral matter, and ii) oil flotation from the slurry. During flotation, gas bubbles collide with and attach to oil droplets which have already been released from the soil particles, and with oily soil particles. The flotation of oil-in-water emulsions in the absence of solids has been studied extensively in the past (Bennett, 1988; Gray et al., 1997; Okada et al., 1990; Pal and Masliyah, 1990). Experiments of oil flotation from oily soil/water slurries are rarely reported in the literature (Hupka et al., 1991), with the exception of a broad literature on oil sand processing (Hupka et al., 1983; Shaw et al., 1994).

A simplified drawing of the phenomena that occur in the flotation of an oil sand particle is shown in Figure 1. Three major steps of the process are represented as i) collision of an oily soil particle with a gas bubble, ii) attachment of the oil lens to the gas bubble, and iii) transfer of the oil from the mineral particle to the gas bubble surface. It is expected that, because of the short contact time between the gas bubble and the oily particle in the flotation of oil-coated mineral particles (usually much less than 1 second), the transfer of oil from the mineral surface onto a gas bubble surface should be spontaneous in order to satisfy the fast kinetics of the flotation process. Whether the transfer of oil from the mineral particle to the bubble can be controlled, and to what extent, cannot be predicted at this moment.

During flotation, the oil-air attachment occurs if repulsive forces (electrostatic in nature) between oil/water and air/water interfaces are not too high, and if steric barriers at the oil/water interface are not signific-icant (Liu et al., 2003). In the absence of these repulsive forces, oil droplet (freely dispersed in water or located on a solid surface) attachment to the gas bubble can be followed by the spreading process and possible encapsulation of the gas bubble by the oil film (Drelich et al., 1995, 1996; Leja and Bowman, 1968). The thermodynamic condition for spreading of oil at the water surface is described by the spreading coefficient (Leja and Bowman, 1968):

The rate of bitumen transfer from a bitumen-coated quartz plate to a gas bubble surface in aqueous alkaline solutions was recorded photographically. During bitumen spreading, a bulk layer followed the formation of thin bitumen films (precursor films). The bulk layer spread at the bubble surface with a velocity of about one order of magnitude less than the velocity of the precursor film. The energy of activation for spreading of the bulk layer varied from about 66 to 123 kJ/mol depending on the stage of bitumen spreading but remained constant at about 105 kJ/mol for the precursor film. Results are discussed with respect to fundamental issues associated with flotation recovery of heavy oils.

On a enregistré photographiquement la vitesse de transfert du bitume d’un plateau à quartz enduit de bitume vers une surface de bulles de gaz dans des solutions alcalines aqueuses. Lors de l’étalonnage des résultats sont examinés relatifs aux questions fondamentales associées à la récupération par flottation des huiles lourdes.

Keywords: bitumen, oil flotation, liquid/liquid spreading, oil sand.

*Author to whom correspondence may be addressed. E-mail address: jdmiller@mines.utah.edu
When the water surface is completely covered. It is only this latter case ($S_{O/W} > 0$), which is considered in this paper, and the emphasis is on the rate of the spreading phenomena.

The rate of liquid/liquid spreading has been analyzed theoretically (DiPietro et al., 1978; Joos and Pintens, 1977; Joanny, 1987; Brochard-Wyart et al., 1996) and studied experimentally (Suciu et al., 1970; Fraaije and Cazabat, 1989; Chalenko et al., 1990; Peterson and Berg, 1986). For example, spreading of low-viscosity hydrocarbons (0.2–3.4 mPas) on a water surface was shown to be a very spontaneous process and is usually completed in less than 10 to 15 ms for drops with a diameter of 3 to 4 mm (Drelich and Peterson and Berg, 1986). These measurements suggest that the spreading of low-viscosity oils on a gas bubble surface would be a phenomenon of minor concern in optimizing the conditions for the flotation of low-viscosity oils. However, this might not be the case for viscous oils, the study of which for viscous bitumen is the goal of this study.

The majority of the work on liquid/liquid spreading has been limited to simple systems involving pure single-component liquids, and multi-component oils have only been used in a few experiments (Peterson and Berg, 1986; Grattoni et al., 2003) despite the fact that such liquids are of great interest from a practical perspective. In this study, we present the results on the rate of high-viscosity oil (bitumen) transfer from a bitumen-coated quartz slide to an air bubble surface that takes place in aqueous alkaline solutions. The observations of bitumen spreading were recorded with a camera attached to a low-magnification stereoscopic microscope. The motivation for this work was driven by practical rather than fundamental needs and was part of research activities to improve the hot-water processing technology for bitumen recovery from Utah oil sands through an understanding of basic separation mechanisms encountered in the sequence of oil sand slurry digestion, aeration, gravity separation, and flotation (Hupka et al., 1987; Hupka and Miller, 1991).

### Experimental Procedure

Toluene-extracted Whiterocks bitumen diluted with 10 wt% kerosene was used in the experiments. The specific gravity of bitumen was determined to be 0.98 to 0.99 (15.6°C) and the viscosity was found to be 32 to 39 Pas at 50°C (Bukka et al., 1992). The detailed chemical characterization of this bitumen is presented by Bukka et al. (1992). Surface tension of bitumen and bitumen/water interfacial tensions at varying pH values are also presented in a previous contribution (Drelich and Miller, 1994).

The quartz plate covered with a bitumen layer (about 1 mm thickness) was placed in a glass cell, filled with a NaOH solution (pH 10), and examined at various temperatures, from about 20 to 46°C, as controlled by a hot plate. Although mild alkaline solutions (pH 8–9) are used in processing of the Utah oil sands (Hupka and Miller, 1991), more alkaline solutions were used in these experiments to maintain a constant pH value over the course the experiment. No significant differences between bitumen spreading at pH ~9 and pH 10 were observed in our preliminary tests. The system was next equilibrated for 15 min. Then, an air bubble with a diameter of 2.5 to 3.5 mm was attached to the bitumen layer using a microsyringe (Figure 2). Bitumen spreading over the bubble was observed and photographed through a stereoscopic microscope (STEMI SV8, Carl Zeiss Jena, Germany). The photographs were taken at precisely timed intervals; lighting allowed for an exposure time of less than 0.5 second. All photographs were taken with the same magnification (14.2 X). The shape of each bubble was assumed to be a spherical cap, and the bubble base diameter (D), its height, and the height of the bubble base zone covered with the bitumen film (h), were measured from photographs with an accuracy of 0.035 mm. The bubble surface coverage by the bitumen film was assumed to be symmetrical and was calculated ($%A$) from a ratio of the bitumen covered area ($A_c$) to the total bubble area ($A_T$). Because attached bubbles had a hemispherical shape, the bubble surface coverage was calculated from the following equation:

$$%A = \frac{A_c}{A_T} \times 100\% = \frac{2h}{D} \times 100\%$$  

### Results and Discussion

#### General Observations

Numerous microscopic observations of bitumen being in contact with the surface of an aqueous phase revealed that the bitumen always tends to cover the water/air interface. The Whiterocks bitumen diluted with 10 wt% kerosene selected for this study is no exception to this rule. Some of such observations made with...
natural Utah oil sands immersed in aqueous phases of varying composition are described in previous publications (Drelich et al., 1992, 1995, 1996; Drelich and Miller, 1994) and showed that bitumen transfer to micro-bubbles occurs at a broad range of pH, temperature, and ionic strength of the aqueous phase. This bitumen-transfer process affects efficiency and rate of bitumen recovery in the hot water processing of oil sands (Drelich et al., 1995). Spontaneous spreading of bitumen over the water/air interface was also reported for Whiterocks bitumen extracted from sand and purified (Drelich et al., 1996). The measurements of surface tension for bitumen and water saturated with bitumen as well as water/bitumen interfacial tension provided convincing proof of a positive spreading coefficient in these systems, the major driving force for the spontaneous bitumen spreading (Drelich et al., 1996).

Figure 3 shows a snapshot of bitumen transfer from a quartz plate to a gas bubble as recorded in this study. Continued observation of the event in Figure 3 would reveal a complete enveloping of the gas bubble with bitumen in the final stage of the spreading process. Examples of photographs showing the spreading of bitumen film on the gas bubble surface at different stages are shown in previous work (Drelich et al., 1995, 1996) and will not be repeated here.

In this study, the influence of temperature on the rate of bitumen spreading was examined. The temperature was controlled in a range of 20 to 46°C. As expected, there was a distinguishable difference between the bitumen spreading at room and elevated temperatures; bitumen spreading occurred much faster and the formed bitumen coating appeared to be thicker at elevated temperatures.

The visual observations revealed what appears to be a fractionation of the multi-component bitumen during spreading into at least three films of varying thickness. A schematic of bitumen spreading and its fractionation is shown in Figure 4. At the base of a gas bubble, bitumen formed a bulk layer (black in color) that spread at a low rate.

Thin bitumen films (precursor films) moved in front of the bulk layer at increased velocity (Figure 4). There were at least two different precursor films, one with a brownish-yellow color having a distinctive front rim whose velocity of spreading was recorded and is reported in this paper. The brownish-yellow color suggests that this film has a thickness of at least a few tenths of a micrometer. Rainbow colors, characteristic of oil films with a thickness of a few micrometers, were also observed on a water surface in front of the brownish-yellow precursor film, indicating the spreading of an additional fraction of the bitumen in front of the precursor film. The rim of the rainbow-colored film could not be clearly identified in this study, and therefore, kinetics of spreading of this microscopic film are not discussed in this paper.

Additionally, a monolayer of selected bitumen components probably preceded precursor films. Other authors (Cazabat, 1987; DiPietro et al., 1978; Leger and Joanny, 1992) have reported the formation of a molecular layer during the spreading of certain oils. Our previous tensiometric studies also suggest the presence of such a monolayer in front of the precursor films that spreads much faster than any film/layer discussed in this paper (Drelich et al., 1996). The molecular layer(s) was also indistinguishable under the stereoscopic microscope, and thus the kinetics of spreading for this layer could not be measured. However, it should be recognized that different mechanisms might govern the spreading of the bitumen monolayer and both precursor film and bulk layer (Cazabat, 1987; DiPietro et al., 1978; Leger and Joanny, 1992). The precursor film spreads very slowly compared to the bitumen monolayer (Drelich et al., 1996); the bulk layer spreads more slowly, as is shown in the next part of this section.

It should be recognized here that although the first precursor film (monolayer) spreads over the clean air/water interface, subsequently spreading of the precursor film(s) and bulk layer occurs at the water surface already covered with the bitumen or its selected fractions (most likely polar components of the bitumen and its light ends).

No measurements of the discrete nature and thickness of spreading layers have ever been performed for systems such as analyzed in this study. In this regard, the overall picture of stratification of a spreading bitumen film as discussed in this contribution must be considered as a rather crude analysis. For example, a discrete structure for the precursor film(s) is not known, but it was observed that these films could exhibit a variation in thickness. Discontinuities in the thickness of the bitumen films have quite frequently been observed in our laboratory during examination of the spreading of bitumen at the water surface (Drelich et al., 1996).

Rate of Bitumen Spreading
The portion of the bubble surface covered by the bitumen versus time of spreading was analyzed at different temperatures.
results followed the trends shown for several temperatures in Figures 5 and 6 for the precursor film and bulk layer, respectively. The accuracy of surface coverage measurements from photographs exceeded 6% but the reproducibility of the rate of spreading was less than 15–20%. Poor reproducibility in recording of bitumen spreading over the air bubble surface was mainly associated with the effect alkaline solution has on waving or even dewetting of bitumen film from the quartz surface and resulting variation of the bitumen film thickness. Also, inconsistencies in preparation of the bitumen films on the quartz plate surface of the same thickness contributed to the variation in amount of spreading bitumen film as well. A variation in bubble size and time required to attach a gas bubble to the bitumen film also had an effect on limited reproducibility of the experimental results. The large error value is reflected in scatter of the experimental data, although the variation has no consequence in the conclusions reached in this paper.

As shown in Figures 5 and 6, the precursor film spread much faster than the bulk film, but both films followed a similar spreading pattern. Specifically, spreading was much faster at the base of the bubble (the beginning of the process) and diminished exponentially with the film’s advance, which is in agreement with observations and discussions reported in the literature for other systems (Cazabat, 1987; DiPietro et al., 1978; Leger and Joanny, 1992). This effect is mainly explained by the diminishing capillary force as the result of decreasing contact angle, approaching an equilibrium value (zero or a close-to-zero value for this system). Saturation of the water surface with surface-active bitumen components released from bitumen and moving in front of the observed spreading films is another primary reason for lowering the driving capillary force through reduction of water surface tension. Also, the bitumen/water interfacial tension is a dynamic property for the time scale of the experimentation performed (Drelich and Miller, 1994).

Linear \( u_L \) and areal \( u_A \) spreading velocities were calculated for precursor film and bulk layer using the following equations:

\[
u_L = \left(\frac{\pi D - D}{2 \arcsin(2b/D)}\right) \frac{t}{b}
\]

\[
u_A = \frac{A_t}{t}
\]

where \( b \) is the base radius of bubble portion uncovered by bitumen; \( t \) is the time.

Linear and areal velocities for both films are presented as a function of time for different temperatures in Figures 7 to 10. As expected, the relationship for both velocities with respect to time and temperature is similar.

As shown in Figures 7 to 10, all calculated velocities decrease rapidly with time, following the power function. These correlations are consistent with the velocity of spreading for low-viscosity hydrocarbon drops on a water surface that was recorded with a high-speed video system (Drelich and Miller, 1999/2000) and, as mentioned above, result from a diminishing capillary force which drives the process.

In the case of film spreading over a bubble there is a limiting factor: After full bubble coverage the film cannot spread anymore, it can only get thicker (unfortunately this change could not be recorded during our experiments, though such a change was observed on a number of occasions). Because of this limitation, spreading at higher temperatures, greater than 40 to 45°C, occurs very rapidly, and only a few measurements could be made. Still, results obtained at conditions much less favorable for spreading (bulk layer, low temperature), when the bubble is not fully covered, are quite comparable (Figures 7–10).

Temperature Effect

Four areas of bubble coverage by the bitumen film (25%, 50%, 75%, and 100%) were selected, and the velocities were interpolated where necessary in order to compare data collected at all temperatures; the results are presented in Figures 11 and 12, for precursor film and bulk layer, respectively. Increase in the precursor-film-spreading velocity is so large with an increase in temperature that, for temperatures over 40°C, practically complete coverage of the gas bubble surface by the spreading film was observed within a few seconds or less. On the other hand, the bulk film did not even reach full coverage at lower temperatures (below 30°C) during several minutes.

Because of the close-to-exponential correlation between linear velocity of spreading for both precursor film and bulk layer and reciprocal of temperature (Figures 11 and 12), the Arrhenius law was used to relate the spreading kinetics and calculate activation energies for bitumen film spreading on the water surface:

\[
u_L(T) = \nu_L(T = 0)\exp\left(\frac{E_A}{RT}\right)
\]

where \( E_A \) is the activation energy for bitumen spreading, \( T \) is the temperature, and \( R \) is the gas constant.

The linear dependence of \( \ln(u_L) \) vs. \( 1/T \) allowed for the calculation of \( E_A \). It was found that the spreading activation energy is independent of the bubble coverage for the precursor film, but decreases as the film advances for the bulk layer spreading (see Table 1). The magnitude of the calculated activation energies is close, but the values are about 50% higher than the results obtained by Chalenko et al. (1990) for spreading of (low-viscosity) 1-decanol on water; their results ranged from 42 to 75 kJ/mol.

The decrease in bitumen viscosity is the main reason for the variation in spreading rate of the bitumen bulk layer with temperature. The viscosity of the Whiterocks bitumen has been reported to decrease with increasing temperature and increasing content of kerosene (Hupka et al., 2003). For example, the viscosity of pure Whiterocks bitumen is about 1100 Pa·s at 30°C and drops to 17 Pa·s at 60°C. The dilution of the Whiterocks bitumen with 10 wt% of kerosene reduces

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Figure 4. Schematic of possible films formed by the bitumen during its spreading over the water surface.
the viscosity of bitumen to about 40 Pa·s at 30°C and 1.6 Pa·s at 60°C (Hupka et al., 2003). The results of viscosity measurements at different temperatures presented by Hupka et al. (2003) were used to calculate the activation energy using an Arrhenius-type formula (4), where linear velocities were replaced with viscosity. The results of $E_A$ are shown in Table 2, and they are values similar to activation energies calculated based on the spreading data. This close agreement suggests that intermolecular forces between bitumen components have a strong effect on the rate-determining mechanism in the bitumen-spreading process.

The process of bitumen spreading involves a complex mechanism that can be divided into at least two stages: (i) accumulation of molecules separated from the bitumen on the water surface and (ii) their movement over the surface of the bubble. Each stage has its own rate, and the slower stage dictates the rate of the overall process. The stage dominating the rate of the process in the case of the precursor film is the accumulation of the molecules; the extension of coverage has no influence on the activation energy. For the bulk film, which is much thicker, the energy decreases with the extent of coverage. This might be associated, as discussed earlier, with a saturation of the gas bubble area by the precursor film(s) in front of the spreading bulk layer, and conditions for the bulk layer spreading are different at the beginning of the spreading process than in its advanced stage.

**Summary**

Because of the short contact time between the gas bubbles and bitumen (in the form of lenses at mineral particle surfaces), the attachment of bitumen to a gas bubble and the kinetics of bitumen spreading over the bubble surface should be rapid in order to guarantee an efficient separation process. The results of this study indicate that the transfer of viscous bitumen from a quartz surface to an air bubble is a relatively slow process at room and moderate temperatures, and, thus, the flotation of viscous bitumen from oil sands might be significantly limited by the bitumen-transfer process. Elevated temperature significantly enhances the bitumen transfer from the quartz surface to the air bubble. In conclusion, reduction of the bitumen viscosity seems to be the way for improved bitumen recovery from oil sands, and this observation is consistent with the technological criteria established in the past (Hupka et al., 1987; Hupka and Miller, 1991).
Microscopic observations showed that the Whiterocks bitumen spreads spontaneously on the surface of the air bubble. It was possible to record the spreading kinetics of the precursor film and bulk layer. The precursor film spread over the air bubble surface with a varying velocity of 0.01 to 0.04 mm/s at room temperature, depending on bubble coverage. At the same temperature, the velocity of the bitumen bulk layer was slower, varying from about 0.002 to 0.01 mm/s at different stages of spreading. The kinetics of spreading for both precursor and bulk films increased by an order of magnitude at about 46°C.

The improvement in the rate of bitumen spreading is even better at temperatures of 50 to 60°C and it took only a few seconds for the bitumen to spread over the gas bubble. Due to this fast rate of bitumen spreading at high temperature, the event of bitumen spreading could not be recorded with acceptable resolution using the simple set-up of this study, a camera attached to a stereoscopic microscope. An additional reason for not recording any data at temperatures higher than 46°C was that the films of bitumen were unstable on the quartz plate in aqueous alkaline solutions and dewetted in seconds to form droplets/lenses with contact angles greater than 150°. The few seconds’ time required for a macroscopic bitumen film to envelop a macroscopic gas bubble at...
elevated-temperature conditions corresponds to the fraction of a second that is needed to transfer 0.1 to 1 μl bitumen lenses formed on the surface of sand grains to 0.4 to 1 mm diameter gas bubbles nucleated in the Whiterocks oil sand slurries during digestion.

The activation energy for spreading of the bulk layer over the air bubble surface was found to vary from 66 to 123 kJ/mol, depending on the stage of spreading. The activation energy for the spreading of the precursor film did not vary appreciably at any stage of spreading and was found to be about 105 kJ/mol. The energy of activation for bitumen spreading was found to be comparable to the values of activation energy of viscous flow calculated from viscosity measurements. This close agreement indicates that strong intermolecular interactions between bitumen molecules reduce the rate of bitumen spreading at the water surface.

**Nomenclature**

- \( A_C \) area of gas bubble covered with the bitumen film, (m)
- \( b \) base radius of bubble portion uncovered by bitumen, (m)
- \( D \) diameter of bubble base, (m)
- \( E_a \) activation energy for bitumen spreading, (J/mol)
- \( h \) altitude of the rim for the precursor film or bitumen layer on the bubble surface, (m)
- \( R \) gas constant \( R = 8.31 \text{ J/(mol-K)} \)
- \( S_{OW} \) spreading coefficient for oil on the water surface, (mN/m)
- \( t \) time, (s)
- \( T \) temperature, (K)
- \( u_a \) areal spreading velocity, \( (m^2/s) \)
- \( u_l \) linear spreading velocity, (m/s)

**Greek Symbols**

- \( \gamma_o \) surface tension of bitumen, (mN/m)
- \( \gamma_{OW} \) bitumen/water interfacial tension, (mN/m)
- \( \gamma_w \) surface tension of water, (mN/m)

**References**


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