The Recovery of Oil from Oil/Sand Slurries in a Laboratory-Scale Flotation Cell

E. V. Lau, K. L. Foo, and P. E. Poh

Abstract—**Oil/sand slurries are found abundantly particularly at petroleum refineries. The ability to recover oil from these oil/sand slurries is an added advantage to meet the increasing need in oil consumption. Thus, this research aims to investigate the effects of temperature and pH in the recovery of oil from oil/sand slurries using the flotation technique. The critical operating temperature and optimum pH condition are determined to be at 50°C and pH 9 respectively, whereby the maximum average oil recovered is 63.2 wt%. Oil recovery is found to be favorable at elevated temperatures due to the reduced oil viscosity which facilitates the liberation of oil from oil sands. Under alkaline conditions, negative surface charge is increased, resulting in increased disjoining pressure between the oil and sand grains which led to the improved oil recovery. Thus, the flotation process provides a promising alternative to recover oil from oil/sand slurries.**

Index Terms—**Beach remediation, flotation, oil spill, pH, temperature.**

I. Introduction

Flotation is a combination of chemical, physicochemical and physical phenomena that govern the three phrase solid-liquid-gas flotation system [1]. The mechanism of a flotation process is fundamentally the generation of small bubbles which can be achieved chemically, by direct addition of gas through porous dispersers [2], by electrolysis [3], through mechanical agitation combined with air injection [4], by direct injection through sparger [5] or by dissolution of air to water through pressure [6], depending on the flotation technique adopted. Flotation exploits the physicochemical surface properties of a substance and has high selectivity of the desired recovery particle. It allows adsorption of the hydrophobic particles to the bubbles generated, whereby the particles attaches to the bubbles as shown in the detailed view in Fig. 1.

The separated hydrophilic material will be left in the pulp to be removed whereas the bubble-particles will float to the surface, creating a froth layer consisting of the separated particles which can then be collected. In the case when hydrophobicity of the minerals or substance is absent, it can be chemically conditioned for the selective separation; therefore flotation is also deemed to be independent of particle properties [7].

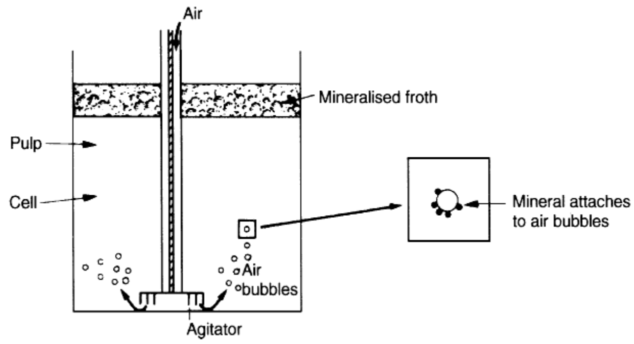

Fig. 1. Illustration of the flotation mechanism

The main underlying mechanisms involved in the flotation process for oil sands are oil liberation, oil-bubble attachment and oil aeration. Physicochemical, interfacial and hydrodynamic conditions were found to play a major role in the liberation and aeration of oil which ultimately affects the oil flotation [8]. The effect of temperature on the overall recovery of oil in oil sands processing have been extensively studied over the years. Operating temperature was determined to be one of the key process variables that play a vital role as the controlling parameter in oil sands processing. To a certain extent, alteration of this parameter would cause adverse change in the flotation yield of oil recovered from oil sands. This is due to its influence on nearly all the properties of oil sands among which includes viscosity, surface tension and bitumen-solids adhesion that impose prominent impact on bitumen recovery [9].

Sodium hydroxide (NaOH) is known to have strong pH-regulating capability and is mostly used for alkalinity control during processing of non-metallic minerals [1]. Besides adjusting slurry pH, the role of base sodium hydroxide addition was found to activate the production of natural surfactants which are also found to be the surface active agents for the process of oil recovery [10]. In a flotation process, the effect of pH is predominantly on the water chemistry of the system. Nonetheless, the impact of alkaline pH on the physical properties of the system such as the interaction forces [11], interfacial tension [12] and electric surface potential [13] were found to substantially improve oil recovery.

Global oil consumption and demand is rising tremendously while its industrial production is running at the expense of dwindling resources. As conventional sources of oil and gas deplete, it is inevitable that oil sands will play a greater role in meeting petroleum needs [11]. In petroleum refineries, a huge amount of oil sludge containing reasonable amount of oil (hydrocarbons) is generated, which merits treatment for oil recovery from an economic point of view [14]. In view of

Manuscript received January 2, 2013; revised April 1, 2013. This work was supported in part by Monash University Sunway Campus under Seed Grant E-10-12.

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DOI: 10.7763/IJESD.2013.V4.369

the promising potentials of oil sands, its oil recovery deserves greater attention in the industry.

Effective technology that can perform separation of in-situ contaminated sediment-oil mixtures is of great environmental significance [15]. The phenomena of flotation are still unpredictable despite its dramatic progress in the past decades and there is still considerable lack of knowledge on the basic principles underlying its operation [1]. As such, this research aims to investigate on the effects of temperature and pH on oil recovery from oil sand slurry by constructing analytical methods for the determination of optimum operating conditions. The findings from this study are analyzed comparatively with the literature researches on bitumen recovery due to the similarity in their composition.

II. Materials and Methods

A. Oil/Sand Slurry

Model oil sand sample is synthesized using sand obtained from a designated site and bunker oil obtained from Shell Malaysia. Dry sieving of sands is carried out using Retsch AS 200 sieve shaker to remove large stones and gravels and for sand particle size distribution. Particle size analysis indicates that 70% of the sands were within the size range of 500µm to 2mm and the mean particle size was found to be 500µm. Fine particles below 125µm were found to be little. 50g of sieved sands was mixed with 20g of oil and the mixture is left to mix homogeneously for one day.

B. Materials

The chemical used to alter solution pH is analytical grade sodium hydroxide solution with concentration of 0.1M obtained from Sigma Aldrich. A known amount of 0.1M sodium hydroxide is added into 250ml of distilled water for pH conditioning of the oil sands. The solution is preheated before adding into the oil sand mixture to form oil sand slurry.

C. Experimental Setup

A laboratory scale setup consisting of a 500ml beaker and a mechanical agitator is used to replicate the actual flotation cell. A hot plate is used to maintain the operating temperature of the mixture at the desired level. The experiments are carried out by stirring the oil sand slurry at an agitation speed of 600rpm for the duration of 10mins. Upon completion of the process, oil-rich froth layer is recovered and filtered onto a filter paper. The filtered bulk of oil is left to dry in a microwave oven for a day to remove excess water content in the recovered oil. The final recovery of oil is weighed using a mass balance.

D. Data Analysis

Mass balance analysis is carried out for the recovered oil. Calculation of oil recovery is done as a percentage of weight, as in (1).

$$Oil\ recovery\ (\%) = \frac{Mass\ of\ oil\ recovered\ (g)}{Mass\ of\ oil\ in\ oil\ sand\ mixture\ (g)} \times 100\% \qquad (1)$$

Regression model of the data is plotted using SigmaPlot to describe the effect of temperature and the effect of pH on oil recovery respectively.

III. Results and Discussion

A. Effects of Temperature

Experimental data for the flotation process at various temperatures at neutral pH were best fitted to a sigmoidal curve as shown in Fig. 2 (coefficient of regression, r^2 of 0.7334). This trend of plot is congruous to the plot for effect of temperature on bitumen recovery found in [9]. The critical operating temperature at 50°C agrees well with [16], who also found that high separation efficiency in general tar sands processing is achieved at temperature of 50-55°C with mild alkalinity. Increasing sigmoid trend is observed for temperatures 30°C to 40°C where the oil recovery increases exponentially. At temperatures above 50°C, the curve for oil recovery as a function of temperature undergoes a deceleration phase and reaches a plateau at elevated temperatures. This is in agreement with literature [9], [15], and [17] that the recovery of oil will not be further affected at temperatures between above 50°C and that oil recovery will level off at elevated temperatures.Standard deviation was found to be higher for temperatures from 50°C to 80°C which could be due to instability of the oil substance when it is heated near or above its flash point of 60°C.

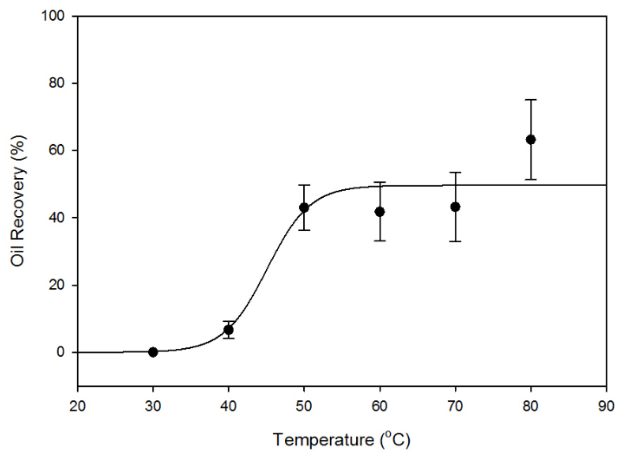

Fig. 2. Effect of temperature on the recovery of oil from oil sand slurry

On a different note, the dynamic viscosity of the oil sample was measured over a range of temperatures as seen in Fig. 3 in order to study the effect of temperature on oil viscosity. The viscosity plot shows a decreasing exponential curve with increasing temperature which corresponds to similar observations by previous researches [9], [15]. As temperature increases, oil viscosity exponentially decays whereas oil recovery exponentially increases until it reaches a climax at 50°C, after which it decelerates to a plateau. Based on the inverse relationship between oil viscosity and its recovery, it is determined therefore that oil recovery ameliorates with decreased viscosity. Thus, this again agrees that the critical operating slurry temperature for the oil sample used in this study is said to be 50°C, below which oil recovery was observed to drastically decrease. Recovery of oil was found to be insignificant and immeasurable at room temperature. The poor recovery is mainly due to the high oil viscosity above 2000mPa.s. Reference [12] discussed that due to the increased viscosity at low temperature, rate of oil film recession is consequently reduced. Liberation of oil from oil sand without the aid of thermal energy would be very difficult because of the existing high viscous force, thus resulting in poor or no separation of oil. This is also in agreement with [15] in that detachment capacity of the oil residing on sand surfaces is enhanced through decreased viscosity by increasing the operating temperature.

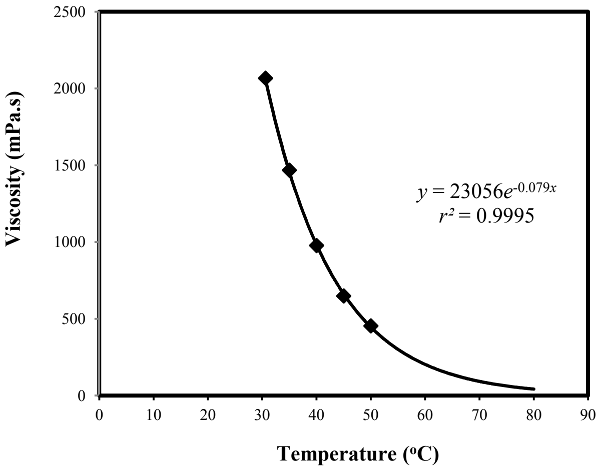

Fig. 3. Effect of temperature on oil viscosity

B. *Effects of pH*

Data from the experiments carried out to study the effect of pH on the recovery of oil at the critical temperature of 50°C were also fitted to a sigmoidal curve as shown in Fig. 4 (coefficient of determination, r^2 of 0.6792). Over the range of pH 6 to pH 9, there is an exponential increase in the oil recovery observed from the plotted data. Substantial increase in oil recovery was observed at pH 9 above which the oil recovery subsequently came to a plateau. The pH value of 9 was determined to be the optimum pH value for the flotation process of oil sands slurry sample in this study. The results obtained in this study agree with [11] whereby flotation pH below 8 will result in a sharp drop in bitumen recovery particularly at low temperatures and that a control of flotation slurry pH by addition of sodium hydroxide is recommended.The bunker oil sample used in this study was determined to be acidic in nature which will therefore result in saponification when reacted with the base sodium hydroxide. Upon saponification, sodium hydroxide reacts with the oil which in turn will cause the release of natural surfactants [13] through pH-induced dissociation of organic acid. Reference [18] identified that the organic acid produced most prevalently the carboxylate surfactant that acts as a surface active agent. Addition of sodium hydroxide therefore is believed to be predominantly for the production of natural surfactant that can influence interaction of oil-water, bubble-water and sand-water, consequently affecting the overall bitumen recovery.

At slurry conditions above pH 9, significant reduction on the surface tension of water and the interfacial tension between oil and water is apparent in that oil was observed to be easily aerated to the surface. This is because at low oil-water interfacial tension, oil can easily spread over the microbubble surface, encapsulating the bubble which is favorable for the aeration mechanism.Under acidic conditions, no observable recovery was obtained after the flotation process for oil sands slurry. The sand particles were observed to be oil-wetted, coated by the oil with no observable liberation of oil from the sand grains. On the other hand, in mild to high alkaline conditions, oil is easily liberated from the sand grains due to the repulsive charge of oil and sand. These observations correspond to that for bitumen pickup test that was carried out by [19] that recorded a maximum coverage of silica sand surface at pH<3 and a minimum at pH>7. Reference [19] also discovered that bitumen surface is more negatively charged than silica surface in pH5. As the pH value increase, bitumen and silica will be more negatively charge which is favorable for the liberation of bitumen from solids as is observed for the experiments that were carried out in this study. Moreover, increased disjoining pressure was evidently observed with increased pH value when oil was more easily separated from the sand grains, thus achieving enhanced oil liberation from sand and improved oil recovery.

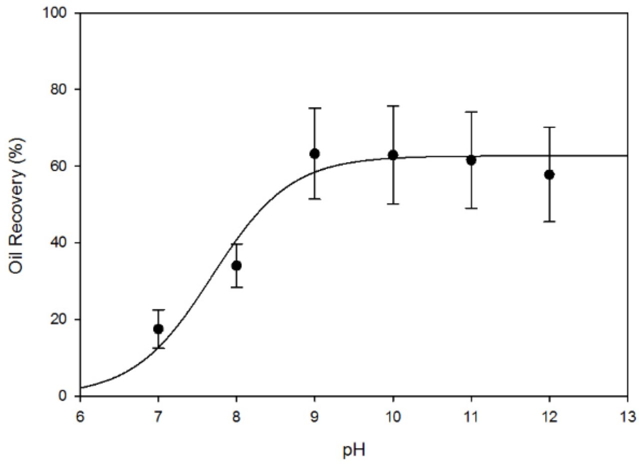

Fig. 4. Effect of pH on the recovery of oil from oil sand slurry

On a different note, the slime coating phenomenon was observed at lower temperatures and low alkaline condition. The slime coating phenomena, as seen in Fig. 5, is the hetero-coagulation of fines or coating of fines on the oil droplet surface, which prevents the oil-bubble contact. This is therefore not favorable for oil aeration and will consequently result in deteriorated recovery of oil. Occurrence of this phenomenon is due the adhesion force of oil and the attractive long-range interaction force inducing a steric barrier that retards the oil-bubble contact [15]. In addition to that, poor froth quality is recovered following the occurrence of slime coating due to the attachment of fines on oil surface.

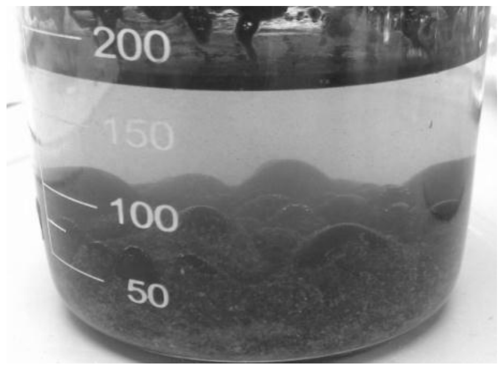

Fig. 5. Slime coating under low alkaline pH condition at temperature of 40°C

IV. Conclusion

Findings from the experimental results iterated the significant influence of temperature and pH on the overall recovery of oil. Elevated temperatures from 50°C to 80°C are found to affect several key process variables which are propitious to the flotation process. Oil viscosity, which is the primary affecting factor for oil liberation, exponentially decreases with increasing temperature. As such, liberation of oil is more spontaneous and apparent at higher temperatures, which is essential for good oil recovery. The threshold viscosity is within the range of 500-650mPa.s below which recovery of oil deteriorates. Moreover, froth layer is thicker at elevated temperatures, indicating enhanced aeration of oil due to the nucleation of micro-bubbles. Test runs carried out in acidic conditions showed insignificant oil recovery, indicating the detrimental effect of acidic pH. As pH increases, adhesion force between oil surfaces is reduced whereas the repulsive charge of oil and sand increases, which favors liberation of oil from sand grains. Oil-water interfacial tension is also reduced under alkalinity due to the weakened adhesion force and adsorption of natural surfactants formed from the reaction of sodium hydroxide with the acid in oil. Thus, attachment of oil with bubble and subsequently the aeration of oil-bubble agglomerates are favored. Critical operating temperature of 50°C and an optimum pH condition of pH 9 are the optimized parameters found to yield enhanced oil recovery from the oil sand slurry samples during the flotation process in this study. The maximum average oil recovery achieved in this study is 63.2 wt%.

References

[1] S. M. Bulatovic, "Summary of the Theoretical Aspects of Flotation," in Handbook of Flotation Reagents: Chemistry, Theory and Practice, Flotation of Sulfide Ores, 1st ed., Elserview B. V., pp. 87-123, 2007.

[2] F. P. Puget, M. V. Melo, and G. Massarani, "Comparative study of flotation techniques for the treatment of liquid effluents," *Environmental Technology*, vol. 33, pp. 79-87, 2004.

[3] X. B. Li, J. T. Liu, Y. T. Wang, C. Y. Wang, and X. H. Zhou, "Separation of Oil from Wastewater by Colum Flotation," *Journal of China University of Mining & Technology*, vol. 17, 4, pp. 546-551, 2007.

[4] J. Rubio, M. L. Souza, and R. W. Smith, "Overview of flotation as a wastewater treatment technique," *Minerals Engineering*, vol. 15, pp. 139-155, 2002.

[5] G. F. Bennett, and R. W. Peters, "The removal of oil from wastewater by air flotation: A review," *Critical Reviews in Environmental Control*, vol. 18, 3, pp. 189-253.

[6] T. R. Rodrigues and J. Rubio, "DAF-dissolved air flotation: Potential applications in the mining and mineral processing industry," *Int. J. Miner. Process.*, vol. 82, pp. 1-13, 2007.

[7] K. A. Matis, G. P. Gallios, and K. A. Kydos, "Separation of fines by flotation techniques," *Separation Technology*, vol. 3, pp. 76-90, 1993.

[8] J. Masliyah, Z. Zhou, Z. Xu, J. Czarnecki, and H. Hamza, "Understanding Water-Based Bitumen Extraction from Athabasca Oil Sands," *The Canadian Journal of Chemical Engineering*, vol. 82, pp. 628-654, 2004.

[9] J. Long, J. Drelich, Z. Xu, and J. H. Masliyah, "Effect of Operating Temperature on Water-Based Oil Sands Processing," *The Canadian Journal of Chemical Engineering*, vol. 85, pp. 726-738, 2007.

[10] L. L. Schramm, and R. G. Smith, "Monitoring surfactant content to control hot water process for tar sand," United States Patent, 5,009,773, 1991.

[11] X. Ding, C. Repka, Z. Xu, and J. Masliyah, "Effect of Illite Clay and Divalent Cations on Bitumen Recovery," *The Canadian Journal of Chemical Engineering*, vol. 84, pp. 643-650, 2006.

[12] J. Drelich, "Wetting phenomena in oil sand systems and their impact on the water-based bitumen extraction process," *Minerals & Metallurgical Processing*, vol. 25, nol. 1, pp. 1-12, 2008.

[13] J. Czarnecki, B. Radoev, L. L. Schramm, and R. Slavchev, "On the nature of Athabasca Oil Sands," *Advances in Colloid and Interface Science*, (114-115), pp. 53-60, 2005.

[14] B. Ramaswamy, D. D. Kar, and S. De, "A study on recovery of oil from sludge containing oil using froth flotation," *Journal of Environmental Management*, vol. 85, pp. 150-154, 2007.

[15] J. Wang, J. Yin, L. Ge, and J. Zheng, "Using Flotation to Separate Oil Spill Contaminated Beach Sands", *Journal of Environmental Engineering*, vol. 136, nol. 1, pp. 147-151, 2010.

[16] J. Hupka, J. D. Miller, and A. Cortes, "Importance of bitumen viscosity in the hot-water processing of domestic tar sands," *Mining Engineering*, vol. 35, no. 12, pp. 1635-1641, 1983.

[17] J. Long, Z. Xu, and J. H. Masliyah, "On the Role of Temperature in Oil Sands Processing," *Energy & Fuels*, vol. 19, pp. 1440-1446, 2005.

[18] M. Misra, R. Aguilar, and J. D. Miller, "Surface Chemistry Features in the Hot Water Processing of Utah Tar Sand," *Separation Science and Technology*, vol. 16, no. 10, pp. 1523-1544, 1981.

[19] Q. Dai and K. H. Chung, "Bitumen-sand interaction in oil sand processing," *Fuel*, vol. 74, no. 12, pp. 1858-1864, 1995.

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