## **PROVISIONAL PATENT APPLICATION - NS305**

# Technique to promote lubrication of bitumen through the addition of colloidal particles in the water by D.D. Joseph<sup>\*</sup> , K.N. Sury<sup>‡</sup> , C. Grant

### Background

When heavy viscous oil is transported through a pipeline, significant energy savings can be achieved by lubricating the oil flow with water as in core-annular flow. Even though the lubricated flow is hydrodynamically stable, oil can foul the pipewall. Sometimes this fouling can build-up to cause increasing flow resistance and ultimate blockage of flow. This issue is the main impediment in commercializing lubricated flow technology.

The present invention specifies that one technique for avoiding fouling is to add colloidal particles of the right type and concentration to the lubricating water. The overall effect of the particles should be to prevent the oil from sticking to itself by covering the oil with a protective coating of particles.

The context for our invention is the need to pipeline bitumen froth economically over long distances (35km). Bitumen froth is produced from the oil sands of Athabasca using the Clark's Hot Extraction process; the froth contains from 20% to 40% by volume of dispersed water in which colloidal clay particles are well dispersed.

The use of clay particles is an embodiment of our invention; it is believed that the same principles apply whenever colloidal particles in water are absorbed on the oil surfaces and act as a barrier preventing droplet coalescence (Tadros and Vincent, 1983).

Significant information exists in the literature on bitumen transport in a core flow mode in which water is added as a lubricant (see Joseph et al. [1997]), but no literature exists on suppression of fouling with a protective coating of colloidal particles or on self lubrication of bitumen froth with dispersed water containing colloidal clay particles. Self lubricated flows are lubricated by the coalescence of some of the dispersed water already in the bitumen and it does not require external addition of water. The present invention is an effective alternative to methods of pipelining viscous oil requiring water addition, and it presents a new strategy for combating fouling.

Bitumen froth is a very special kind of multi-phase material. It combines properties of an oil continuous phase in which water is the dispersed phase with properties of a water continuous phase, like oil-in-water emulsions. In the usual oil-water mixture, dispersions of 20-40% water-in-oil are very stable and very viscous with viscosities even higher than the oil alone. However, the froth is unstable to faster shearing which causes produced

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water droplets to coalesce and form a free lubricating layer of free produced water. In fact, tests indicate a tendency for droplets of produced water to coalesce even under static conditions.

The unusual properties of bitumen froth with respect to the coalescence of water droplets leading to self-lubrication has everything to do with the fact that the produced water is a dispersion of small clay particles in the water. The produced water is not clear, but has the gray color of clay which can be called milky. The milky appearance is persistent because the small particles are colloidal size  $O(\mu)$ , held in suspension by Brownian motions. The free milky water is roughly 20-30% by volume of the original water dispersed throughout the sample; the volume fraction of the free water relative to weight of the mixture defining the froth core is just a few percent.

The clay water inhibits the coalescence of bitumen froth and promotes the coalescence of clay water drops through a mechanism which can be called "powdering the dough". Dough is sticky, but when you cover it with flour powder, the dough loses its stickiness and is protected against sticking by the layer of powder. The clay in the produced water is just like powder; it sticks to and prevents the bitumen froth from coalescing. Zuata crude is much more sticky than bitumen froth and it sticks strongly to glass and plastic bottles filled with water, but not when filled with Syncrude's produced water. Bottles filled with Zuata in the presence of clay water would readily empty without stain when turned upside-down; this is very remarkable and totally unexpected.

The action of the clay particles is very much like the action of surfactants which are used to stabilize emulsions. Yan and Masliyah [1994] have investigated the absorption and desorption of clay particles at the oil-water interface. They note that it is generally accepted that hydrophilic particles (clay) stabilize oil and water emulsions while hydrophobic solids stabilize water-in-oil emulsions. The fine solids absorbed on the droplet tend to act as a barrier, protecting the oil droplets from coalescing with one another. They studied the effect of kaolinite clay particles on stabilization of oil in water emulsions using a multilayer absorption model. As in the theory of absorbed surfactants, absorption isotherms relating the bulk concentration to the surface excess are important. They note that "....To obtain a stable solids-stabilized oil in water emulsion, it is necessary for the droplets to be covered by at least a complete monolayer of particles". This is like the CMC in which the interface is fully saturated and cannot absorb more surfactant. Obviously, enough clay must be in the water to fully cover the drop surface, to powder the dough.

The water droplets are strongly stretched by shear forces at the wall. The froth which is protected by absorbed clay particles is also stretched, but it cannot coalesce or pinch off the droplets because of the protective particle layer. This promotes the coalescence of the extending droplets of produced water into sheets of lubricating water. The annulus of produced lubricating water can work perfectly well between "powdered" froth layers since these protected layers will not coalesce when touching. The bitumen froth may therefore foul the pipe wall with a light layer of froth and still not interfere with the smooth lubrication of the froth core because there is no accumulation of fouling.

The idea suggested by self lubrication of froth in clay water is that fouling of pipe walls by heavy oils may be relieved by adding hydrophilic solids of colloidal size to the water in a concentration above that necessary for saturation of the oil water interface. The same type of colloidal particles which stabilize oil in water emulsions (Tadros and Vincent [1983]) are believed to be effective for reducing fouling. The particles must be hydrophilic, so that a water layer will be retained between protected bitumen in touching contact, as in particle stabilized oil-in-water emulsions. However, the particles cannot be so oleophobic that they will not stick to the bitumen. Additives may be used to create optimal conditions. For example, Yan and Masliyah [1996] have shown a significant effect of the pH in water on the absorption of clay-on-oil in oil-in-water emulsions.

#### Summary

The reduction of fouling of a pipewall by very viscous oil is promoted by the protective coating of the oil by small particles. For example, one way of preventing fouling is through the use of appropriate amounts of water with dispersed clay. Bitumen froth contains about 20 to 30% water in which small clay particles are well dispersed. The froth is unstable to shearing which leads to the coalescence of a portion of the water droplets to form a lubricating layer of free water. The clay-containing water inhibits the coalescence of bitumen froth, and promotes the coalescence of clay water droplets through a mechanism called "Powdering the dough". The analogy is that bread dough is sticky, but when flour is spread on it, the dough loses its stickiness. The dough is protected from sticking by a layer of powder. The clay in the produced water acts like flour, it sticks to and prevents the bitumen in froth from coalescing. The role of the clay particles resembles the role of surfactant in stabilizing emulsions. The fine solids surrounding an oil droplet tend to act as a barrier protecting the droplets from coalescing with one another. Thus the fouling of a pipewall by heavy viscous oil may be relieved by the addition of hydrophilic solids of colloidal size to the water in a concentration above that necessary for saturation of the oil water interface. Moreover a pipe lightly fouled with protected oil would act to protect the fouled wall from further fouling. This is a novel concept.

#### Description of the specific embodiment

The specific embodiment of this invention is realized on successful experiments on selflubrication of bitumen froth run on a one-inch diameter pipeloop set up at the University of Minnesota, on a 2-inch diameter pipeloop at Syncrude's hydraulic test facility and Syncrude's [1996] pilot study in a 24-inch  $\times$  1km pipeloop. (These results are summarized in an internal Syncrude report, "Self-lubricated transport of bitumen froth", which is attached to this document.)

**Example 1:** An example of absence of pressure buildup in the 1-inch diameter  $\times$  20ft long pipeline at the University of Minnesota is found in the results of test 3. Test 3 was a 96-hour test of froth pumping in a continuous operation. There was no buildup of fouling; the pressure gradients did not increase. The test started in a pipeline fouled from previous tests; flushing the pipeline with tap water did not remove the fouled oil on the wall. Figure 1 shows that the measured pressure at each tap is essentially the same for interval (a) and (c).  $\Phi$  is the volume fraction of the water.

The pressure gradients obtained during this test were nearly constant, as illustrated in figure 2. The transients which are induced by taking samples from the pipeline are short lived. These features show that the buildup of pressure, which would occur if there was an accumulation of fouling, does not occur.



Figure 1. Comparison of the pressure history at each pressure tap for tests 3(a), 24 hours and 3(c), 5 hours.  $P_0$  is the pressure at the pump outlet and  $P_1$ ,  $P_2P_3$ ,  $P_4$  are located on the line. In this case,  $\Phi=27\%$ , U=1.0 m/s and  $\theta=35$ °C. There is no evidence of increasing pressure gradients over time.



Figure 2. Dimensionless pressure gradient  $\frac{\Delta P}{L\rho g}$  history between two consecutive pressure taps in the forward • and return • legs of the pipeline for test 3 (b).  $L_1 = L_2 = 3.96$  m. In this case,  $\Phi = 27\%$ , U = 1.5 m/s and  $\theta = 37^{\circ}$ C.

At the end of interval (c) the velocity was dropped to 0.5 m/s, but the pressure was so unstable, that after 20 minutes we raised it to 0.75 m/s; pressure  $P_o$  at the pump outlet jumped to 100 psi and the pipeline strongly vibrated, driven by pressure oscillations. The speed was then immediately raised to 1 m/s. The transient pressure  $P_o$  at the outlet rose to 200 psi and the pressures along the line were over 100 psi. This indicates some partial blockage. After five minutes, the pressures reduced to normal values, 40-45 psi, at the pump outlet and the speed was raised to 1.25 m for m/s and kept for 19 hours. Then it was raised again to 1.75 m/s for other 19 hours.

Figure 3 shows the pressure distribution along the pipeline, parametrized by the velocity U for test 3. Mean values of the pressure were calculated for each tap at each velocity. The average temperatures of the froth increased because of the frictional heating to around 42°C. It is possible that some free water is reabsorbed into the froth at high temperatures as has been suggested by Neiman [1986], who found that heating and water-dilution affect the lubricating layer. Heated and unheated froth possessed a similar headloss, which hardly changes, when the total separable water content in the froth is increased above 35%.



Figure 3. Pressure distribution along the pipeline, parametrized by the velocity U for test #3, 96 hours.  $P_0$  is the pressure at the pump outlet and  $P_1$ ,  $P_2P_3$ ,  $P_4$  are located on the line, so  $P_1$  corresponds to the tap closest to the pump and  $P_4$  to the farthest. In this case,  $\Phi=27\%$  and  $\theta$  varied from 35 °C, for U=1.0 m/s to 42 °C, for U=1.75 m/s.

The water content of the froth used in test 4 is the highest ( $\Phi$ =40%) of all the samples tested. The dimensionless pressure gradient record (included in an internal report) for this watery sample shows more erratic behavior than less watery samples. However, the pressure levels are roughly those of other samples with different water contents. Moreover, in this test and all the others, there is again no evidence of a systematic increase of pressure which could indicate accumulation of fouling.

#### **Example 2:** Pilot scale tests

The pilot tests were in a 24-inch (0.6m) diameter, 1000m long pipeloop at Syncrude's operation in Ft. McMurray, Canada. A narrative of tests results will now be given. The pipeloop was filled with water prior to the start of froth pumping. The froth pump drive speed was initially set at 650 rpm to obtain a froth flow velocity of about 1.0 m/s. As the froth displaced the water in the pipeline, the pump discharge pressure increased. It took about 10 minutes to displace the water completely and to establish the core-annular flow. To ensure stable flow, the pump drive speed was gradually increased to 800 rpm. As the pump speed increased, the pump discharge head was well below that required for pumping water at similar flow rates. This operational setting was continued without change for about 24 hours. During this period, the pressure and flow readings were monitored.

There was no continuous increase of the pressure drop and other bitumen fouling related problems in the line. However, both froth temperature  $(43^{\circ}C \text{ vs. } 47^{\circ}C)$  and velocity (1.10-1.14 m/s vs. 0.90 m/s) decreased for a fixed pressure drop across the loop as the night approached.

In another test core annular flow at a temperature of about 55°C was readily and predictably established in 10 minutes. The initial pump drive speed was set at 650 rpm and the froth flow velocity was maintained at about 0.9 m/s for 2 hours of steady operation. Then the pump drive speed was raised and lowered gradually from 650 rpm to 1000 rpm and back in steps of 50 rpm. At each speed, pressure and flow readings were monitored for about 10 minutes and the test ran for 2 hours. There was no hysteresis observed either in the velocity or pressure.

**Example 3:** The concept of protection against pipe wall fouling was verified in emptying tests from cylinders on a bench comparing clay water from Syncrude's tailing pond and tap water with bitumen from two sources, namely, Syncrude bitumen froth and Zuata bitumen from Venezuela. The bitumen was loaded into the water cylinder and left to rest, then emptied. The walls of the vessel never fouled when tailings water was used, but did foul when tap water was used. A videotape of this experiment is available.

**Example 4:** In another experiment it was verified that the clay water promotes lubrication of *froth* from *froth*. Bitumen froth was sheared between two 3-inch (75mm) diameter glass parallel plates. One plate was rotating and the other was stationary; water was released inside, fracturing the bitumen. The internal sheet of water was sandwiched between two layers of bitumen, which stuck strongly to the glass plates. The bitumen on the moving plate rotated with the plate as a solid body. The froth fractured internally as a cohesive fracture and not as an adhesive fracture at the glass plates. Some of the water in the sandwich centrifuged to edges. A videotape of this experiment is available.

**Example 5:** Data from all experiments using Syncrude's froth are summarized in figures 4 and 5. The reduction of the pressure gradient that can be maintained by the addition of colloidal clay to the water dispersed in the bitumen froth is 10 to 20 times or less than that for water alone when the froth temperature is between 49° to 50°C and 10 to 40 times or less than water alone when then temperature is between 35° to 47°C; the higher temperature gives a larger reduction of pressure (figure 4). The reduction of the pressure gradient appears to undergo a dramatic decrease at a critical value of the velocity which is believed to be about 1.6 m/s. After this, the mass flow of oil can be increased for only marginal changes of the pressure gradient (figure 5).



Figure 4. Pressure gradient of bitumen froth  $\beta$  [Kpa/m] as a function of the ratio of the 7/4th power of the velocity to the 4/5th power of the pipe radius, parametrized by temperature. Left: 24"(0.6m) diameter pipeline; middle: 2"(50mm) diameter pipeline (Niemans' data); and right: 1"(25mm) diameter pipeline. (a) All available data. (b) Fittings parallel to the Blasius correlation for turbulent pipeflow (bottom line), for two temperature ranges: 35-47°C (top) and 49-58°C (middle). Most of the 2"(50mm) diameter pipeline data was ignored in these fits, due to its high scatter.



Figure 5 Pressure gradient of bitumen froth  $\beta$  [Kpa/m] as a function of the ratio of the 7/4th power of the velocity to the 4/5th power of the pipe radius, parametrized by velocity. Left: 24"(0.6m) diameter pipeline; middle: 2" diameter pipeline (Niemans' data); and right: 1" diameter pipeline. (a) All available data, enclosed by the most pessimistic (i) and least pessimistic (ii) predictions for  $\beta$  based on Blasius' formula, and ignoring the scatter in the 2"(50mm) diameter pipeline data region . (b) I and II are predicted pressure gradients  $\beta$ , based on a velocity criterion, for the 24"(0.6m) diameter pipeline data and 1"(25mm) diameter pipeline data, respectively. Here the critical velocity is approximately  $U_c = 1.6$  m/s.

## Claims

Successful protection of pipelines against fouling means that self lubricated flow can be maintained at reduced pressure gradients over time without further addition of water (figure 4). For successful protection of self lubricated flow of water-in-oil emulsions

- 1. Hydrophilic particles should be dispersed in the water
- 2. The particles should readily stick to the oil
- 3. The particles should be in a concentration in the water sufficient to cover the bitumen with at least a monolayer of particles (Yan & Masliyah, 1994)
- 4. The reduction of the pressure gradient that can be maintained by the addition of colloidal clay to the water dispersed in a bitumen froth is 10 to 20 times or less than that for water alone when the froth temperature is between 49°-58°C, independent of pipe diameters.
- 5. The reduction of the pressure gradient that can be maintained by the addition of colloidal clay to the water dispersed in a bitumen froth is 10 to 40 times or less than that for water alone when the froth temperature is between 35° to 47°C, independent of pipe diameter (figure 4).
- 6. The pressure gradient associated with self-lubrication using colloidal clay in the dispersed water scales with the ratio of the  $\frac{7}{4}$  power of the velocity to the  $\frac{5}{4}$  power of the pipe (figure 5).
- 7. At higher velocities greater than 1.6 m/sec, a further reduction in the pressure gradient than that specified in claim 6 can be achieved.

#### Advantages

The advantage of promoting the lubrication of bitumen through the addition of colloidal particles in the water is in the reduction of fouling leading to reduction of pumping power necessary to overcome frictional losses. The specific realization of these savings is for bitumen froth from the oil sands. In this case, the clay water is produced naturally in the froth and costly additional water injection is not required; the bitumen froth enters into self-lubricated flow. The data for self-lubricated flow follows the Blasius law for turbulent flow with the wall shear stress given by

$$\tau_w = \frac{K}{2} \frac{U^{7/4}}{R_o^{3/4}} = \frac{\beta R_o}{2}$$
(1)

where *U* is the froth velocity,  $R_o$  is the pipe radius, and  $\beta$  is the pressure gradient. Figure 5.1 shows that the pressure gradient for bitumen froth is 10 to 20 times the pressure gradient for water alone when the froth temperature lies between 49°-58°C and between 10 to 40 times the pressure gradient for water alone when the temperature is between 35° to 47°C. This is a pressure gradient of the order of 1000 times smaller than the pressure gradient which would be required if the flow was not lubricated and pipewall fouled with bitumen.

Figure 5 gives the same data sorted by velocity and it shows that when the velocity reached a critical velocity which is believed to be about 1.6 m/sec, the pressure gradient grows much more slowly than is required by equation (1).

#### References

- Tadros, T.F., Vincent, B. in P. Becher, (Ed.), (1983) "Encyclopedia of Emulsion Technology", Dekker, New York, 1: 272.
- Joseph D.D., Bai R, Renardy Y., (1997) Core-Annular Flows. Annual Review of Fluid Mechanics 13, 739.
- Nieman O., (1986) Froth pipelining tests. Syncrude Canada Research and Development Progress Report,. 15(1):373-407.
- Yan N., Masliyah J.H., (1994) Adsorption and desorption of clay particles at the oil-water interface. J. Colloid Interf. Sci. 168: 386.
- Yan N., Masliyah J.H., (1996) Effect of pH on the adsorption and desorption of clay particles at oil-water interface. *J. Colloidal Interf. Sci.*, **181**: 20.