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PRODUCTION OF BOILER FEED QUALITY WATER FROM BITUMEN/HEAVY OIL  
- WATER EMULSION BY ULTRAFILTRATION

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PRODUCTION OF BOILER FEED QUALITY WATER FROM BITUMEN/HEAVY  
OIL - WATER EMULSIONS BY ULTRAFILTRATION

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In order to reduce the large water demand of enhanced bitumen/heavy oil recovery operations, the use of porous membranes in a water recycle process using wellhead oil in water (o/w) emulsions was studied. The permeate was of sufficient quality for single pass steam raising for well injection. However, stable wellhead o/w emulsions were destabilized by this process, which would aid in further processing to make pipeline quality crude oil. Polar material in the membrane permeate was considered to be the stabilizing agent whose removal caused the emulsion's destabilization. Selective removal of stabilizing agents with subsequent destabilization of produced bitumen/heavy oil o/w emulsions has not been previously reported and attempts were made to characterize the polar material. The major difficulties with the use of membranes in this process are severe fouling of the membrane caused by the bitumen and operation at wellhead temperatures.

## INTRODUCTION

The amount of water required for enhanced oil recovery (EOR) of heavy oil and bitumen with steam floods and other water dependent fluid methods is so large that it may become the restricting factor for development of some projects (1). Also, methods of EOR and in situ recovery produce stable wellhead oil-in-water (O/W) emulsions which resist conventional treatment and can be processed only at great expense by chemicals or energy intensive treatment units (1-6). Even with existing specialized steam generation facilities the production of steam from produced water is difficult and accounts for only a small amount of EOR and in situ steam supply (3, 7-9).

Previous work in our laboratory has demonstrated the possibility of using porous membranes as a physical method of breaking bitumen/water emulsions in a batch process to produce high quality water (10). This report is an extension of the previous work to a quasi-continuous membrane process with analysis of the permeate for boiler feed quality parameters. The emulsion used to demonstrate this was a wellhead bitumen/water/mineral emulsion of approximately 4% bitumen supplied by Texaco Canada Resources Ltd., from a steam flood in situ pilot plant at Fort McMurray, Alberta. This wellhead emulsion is currently treated by adding chemical demulsification agents at elevated temperatures (3). Further processing is concerned with producing low water content bitumen with little emphasis on the product water quality.

The use of porous membranes for breaking O/W emulsions is not unique; trade literature and scientific literature are available (11-14). However, no reports exist on the treatment of bitumen/water emulsions with porous membranes. This could be a result of the unusual properties of the bitumen/water emulsions related to the presence of clay, other minerals, water, and dissolved species including salts. The effect of clay on stabilizing O/W emulsions has been demonstrated by Gewers with Athabasca bitumen and he has indicated that this effect is reduced at pH 7 to 8 (6). Broughman reports the density of bitumen and water overlaps at 34°C and 115°C, with water slightly denser between these two temperatures (15). He also reports that this difference is maximized from 65°C to 80°C. With this information, operating conditions for Athabasca bitumen/water/mineral

separations should be at pH 7 to 8 and temperatures from 65°C to 80°C. Although the pH range is acceptable for the membrane used in this work, the temperature range is the extreme of usual membrane practice. The emulsion as supplied was pH 7.

Parameters describing the quality of boiler feed water for several types of steam generation have been summarized by Fulton as shown in Table 1 (9). Although the Thermosludge Generator has lower water quality standards, it also has higher capital and operating costs than a once-through steam generator. For this reason, the once-through generator's standards were considered a test of any water recycle process. Other water standards have been included in Table 1 for comparison.

## EXPERIMENTAL

Unlike the previous work (10), a continuous system for the evaluation of membrane performance was assembled as shown in Fig. 1. When operating with the emulsion, there was considerable difficulty in controlling the operating pressure, which was apparently caused by free bitumen "slugging" through the back pressure control valve. This caused rapid but small variations in the operating pressure which were visually averaged to determine the system's operating pressure. As well, the emulsion was opaque and the rotameter shown in Fig. 1 was not used in the emulsion experiments. For the elevated temperature experiments, no attempt was made to insulate the system from the surroundings, and heat was only applied to the reservoir. Accordingly, the reservoir's temperature was 75°C and the liquid's temperature at the end of the series of cells was 45°C. The latter was considered more significant because of the large amount of tubing and fittings between the reservoir and the first membrane cell.

The experiments were conducted in the following order. First, a pure water permeation (PWP) experiment was performed to determine the PWP rate for each membrane, followed by the replacement of the pure water with KI solution. The permeation rate (PR) of the KI solution experiment was determined for each membrane, and the concentration of KI in the permeate and the reservoir was measured. A function describing the separation is defined as:

$$f = \frac{\text{reservoir concentration} - \text{permeate concentration}}{\text{reservoir concentration}} \quad (1)$$

where  $f$  is the fraction of separation and is expressed as a percent.

The second step consisted of replacing the KI solution with the bitumen/water/mineral emulsion. The PR was determined, and the permeate was analyzed for total dissolved solids (TDS), metals (Mg, Ca, Fe), silica, and pH. The feed solution consisted of 2 L of emulsion, and was not adjusted throughout this step. The third step consisted of replacing the emulsion in the reservoir with a new sample and performing the experiment as in the second case, except the temperature was increased to 75°C in the reservoir and 45°C for the membrane cells.

All of these experiments were performed at 1800 kPag operating pressure and with a circulation rate of 0.5 L/min. The pressure drop throughout the cells at this flowrate was less than 30 kPa, and constant operating pressure was assumed.

## RESULTS AND DISCUSSION

The characterization of the membranes is given in Table 2 with typical KI solution experimental results. The degree of separation is considered inversely proportional to the pore size of the membranes. This assigns the cellulose acetate (CA) membrane the smallest pore size, and the nitrocellulose (NC) or the polytetrafluorethylene (PTFE) membranes the largest pore sizes. It should be noted that heat treatment usually reduces the pore size of polymeric membranes. A wide range of pore sizes was made available for this study in order to evaluate membrane facility for the removal of dissolved species from the permeate. The penalty for small pore sizes is reduced permeation rate, although this is mitigated by the "population" of pores which is considered a function of the membrane fabrication method, membrane material morphology, and molecular weight.

The variation of permeation rates (corrected to the equivalent of 25°C operating temperature) with time is shown in Fig. 2 for the two operating temperatures (25°C and 45°C). This figure demonstrates the large

decrease of permeation rate that occurs when the bitumen/water/mineral emulsion is broken on membrane surfaces. The exception to this is the regenerated cellulose (RC) membrane permeation rates. While a slight decrease of permeation rate was observed for the two RC membranes during the 25°C experiment, they did not suffer the drastic decreases observed for the other membranes. This ability of cellulose membranes to resist organic component fouling has been reported elsewhere (16). However, operating at 45°C caused a large decrease in permeation rate for all membranes. Because of this, this temperature is not desirable for the long term use of the membrane types studied.

In general, the appearance of the permeates was clear with varying degrees of amber colour, and the intensity was approximately inversely proportional to the KI solution. There was no detectable odour, and no evidence of sediment even on long standing, although there was evidence of long-term bacterial activity. As well, the permeate supported a large foam formation when it was shaken. More specific analyses are shown in Table 3 and the limits for single pass boiler feed water of Table 1 are included for comparison. In all cases, TDS passes the limits set in Table 1. However, the PTFE membrane exhibited unusual two-phase permeation for the 45°C experiment, and demulsified bitumen could be observed in the permeate as 2 to 3 mm diam droplets. This phenomena could be the result of the large pore size of the membrane combined with the strong preferential sorption of the bitumen on the PTFE surface.

To confirm that bitumen did not pass through to the permeate (the PTFE case excluded), attempts were made to extract the permeate with toluene. There was no evidence of the transfer of coloured material from the aqueous to the organic phase, nor was there any visible residue left by the evaporation of the toluene suggesting that the material is highly polar. To further evaluate the composition of the various liquid streams, infrared analyses of the aqueous samples for the cellulose acetate case was investigated by their evaporation onto polycrystalline zinc sulphide plates (IRTRAN, Perkin-Elmer) at 50°C with subsequent drying at 105°C in a vacuum oven for one half hour.

The infra red spectra of the bitumen from the emulsion as received and of evaporation residue of the permeate are shown in Figure 3. The former is characteristic of bitumen while the latter bears little resemblance to the former. Thus, the material in the permeate which appears to be the

surfactant that stabilized the emulsion is very different to the bitumen. Acidification of the permeate to pH2 caused the formation of precipitates. Studies on characterizations of this material are in progress.

An unexpected effect of the membrane process was the separation of the emulsion in the reservoir to form two layers: bitumen rich and water rich. The bitumen-rich layer floated as scum on the surface. This layer was retrieved and analyzed for water content by Dean and Stark analysis. The ~~bitumen~~<sup>water</sup> content was 23% at 25°C and 35% at 45°C. Since this effect was unexpected, the retrieval of the bitumen-rich layer may have incorporated water-rich emulsion into it. No attempt was made to measure the rate of accumulation of this layer. However, the instability of the remaining water-rich emulsion was evident as it continued to break down at room temperature to a very dark bitumen-rich layer on the bottom and sandy/muddy brown water layer with visible large particles. The original emulsion as received did not segregate to the same extent.

On this basis, it is possible that the polar material observed in the permeate was the stabilizing agent for the bitumen/water/mineral emulsion, and its removal would cause this segregation. This effect has been described by Gewers (6), where the increase in stability of Athabasca bitumen is enhanced by the presence of asphaltenes and other polar material, as observed by infrared analyses.

Analysis for the concentration of selected metals in the permeates is reported in Table 3. Low concentrations of these metals were observed with the exception of Si, although the CA membrane met the requirements of Table 1 and most of the others were close to this requirement. For Fe, the detection limit for the ion inductively coupled plasma (ICP) analysis is 0.118 ppm, which is greater than the limit given in Table 1. Although the exact concentration of Fe for these permeates was not measured, it is at least in the same range as the limit in Table 1; it is assumed that further refinement of the process will give satisfactory levels.

#### CONCLUSIONS

The use of porous membranes can be considered for the production of boiler feed quality water from bitumen/water/mineral emulsion obtained from the Texaco Athabasca site. The use of a continuous membrane process is possible as demonstrated by this work. An associated difficulty caused by the emulsion is membrane fouling, although the RC membranes do not foul to the same extent.

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Table 1 - Water quality objectives for steam generation and other uses (9)

Parameter	Once-through steam generator <sup>d</sup>	Thermosludge generator <sup>a</sup>	Deep Well disposal <sup>b</sup>	Irrigation	Cooling water make-up
Total hardness, mg/L as CaCO <sub>3</sub>	0.5	100-2000	-	-	c
Silica, mg/L	50	10-250	-	-	c
Oil, mg/L	1	50-1000	20	5	1
TDS, mg/L	8000	1000-50000	-	1000	-
Suspended solids, mg/L	0	10-500	5	-	d
Dissolved O <sub>2</sub> , mg/L	0.04	-	-	-	-
Iron, mg/L	0.05	-	-	-	-

a These are vendor recommendations. Some of these values have been exceeded in actual practice(9).

b Water should be chemically compatible with formation waters.

c The product of Mg as CaCO<sub>3</sub> x SiO<sub>2</sub> should be less than 35,000 mg/L.

d Total suspended solids in the recirculating water should be less than 200 mg/L.

Table 2 - Membrane performance at 1800 kPa and 24°C with dilute KI solution

MEMBRANE NO.:	1	2	3	4	5	6
Material <sup>a</sup>	NC	PTFE	RC	NC	RC	CA
Pore size, m x 10 <sup>10</sup>	100	200	50	50	50	-b
Supplier	Sartorius	S and S	S and S	S and S	S and S	CANMET
Heat treatment °C x 10 min	80°C	80°C	-e	90°C	80°C	-e
(PWP) <sup>f</sup> , avg. g/h	63.43	27.75	5.14	49.18	4.86	38.57
(PR) <sup>f,g</sup> , g/g/h	63.09	24.94	5.35	50.15	5.04	37.94
f <sup>g</sup> , %	7.3	7.3	12	12	20	32

<sup>a</sup> NC = Nitrocellulose; PTFE = Polytetrafluorethylene;  
RC = Regenerated Cellulose; CA = Cellulose Acetate.

<sup>b</sup> = undetermined

<sup>c</sup> S and S = Schleicher and Schuell

<sup>d</sup> CANMET = Fabricated in-house

<sup>e</sup> No heat treatment was applied

<sup>f</sup> Surface area of  $1.26 \times 10^{-3} \text{ m}^2$

<sup>g</sup> Calculated separation (eq 1) for a feed of 2050 ppm of KI

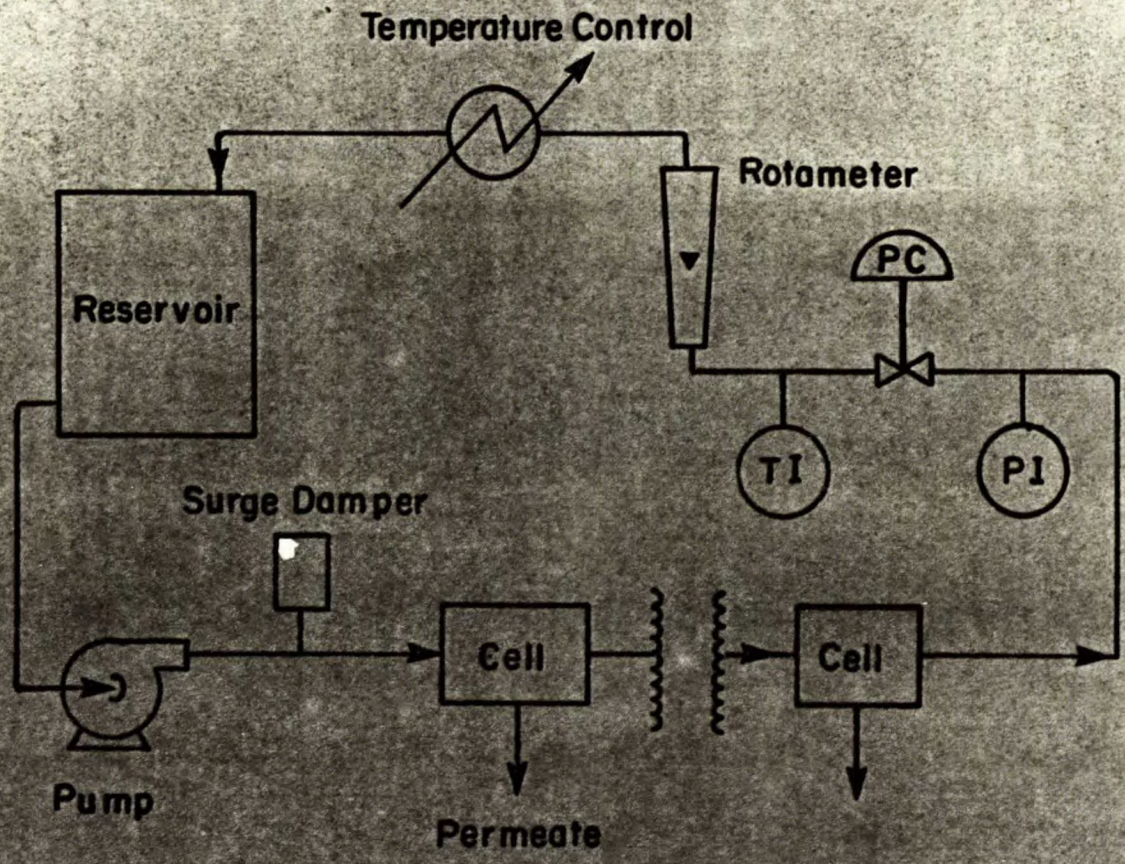
B.F.

Table 3 - Analysis of Permeate for the membranes of Table 2

MEMBRANE NO.:	1	2	3	4	5	6	Limit from Table 1	Original emulsion
Material/ heat treatment	NC/ 80°C	PTFE/ 80°C	RC	NC/ 90°C	RC/ 80°C	CA	-	
<u>24°C Run</u>								
TDS, ppm	635	740	506	738	661	371	8,000	55,000
Ca, ppm	0.07	-	0.07	0.07	0.07	0.07	-	1.8
Mg, ppm	0.15	-	0.15	0.15	0.15	0.15	-	0.45
Fe, ppm	0.12	-	0.12	0.12	0.12	0.12	0.05	4.7
SiO <sub>2</sub> , ppm	63.3	-	59.8	63.2	56.6	39.4	50	157
Suspended solids	none	none	none	none	none	none	0 mg/L	yes
Suspended oil	none	none	none	none	none	none	1.0mg/L	yes
pH	7	7	7	7	7	7	-	7
Total hardness as CaCO <sub>3</sub> , ppm	0.18	-	0.18	0.18	0.18	0.18	0.5	4.6
TOC, ppm of C	45.6	76.8	81.4	69.0	65.0	48.3	-	4%
<u>45°C Run</u>								
TDS, ppm	431	NA	771	-	755	173	8,000	55,000
Ca, ppm	0.07	1.62	0.07	-	0.07	0.07	-	1.8
Mg, ppm	0.15	0.52	0.15	-	0.17	0.15	-	0.45
Fe, ppm	0.12	2.75	0.12	-	0.12	0.12	0.05	4.7
SiO <sub>2</sub> , ppm	59.6	85.3	54.9	-	58.2	26.4	50	157
Suspended Solids	none	-	none	-	none	none	0 mg/L	yes
Suspended oil	none	visible	none	-	-	none	1.0 mg/L	yes
pH	7	7	7	-	7	7	-	7
Total hardness as CaCO <sub>3</sub> , ppm	0.18	4.1	0.18	-	0.18	0.18	0.5	4.6
TOC, ppm of C	50.1	-	63.9	-	61.3	35.5	-	4%

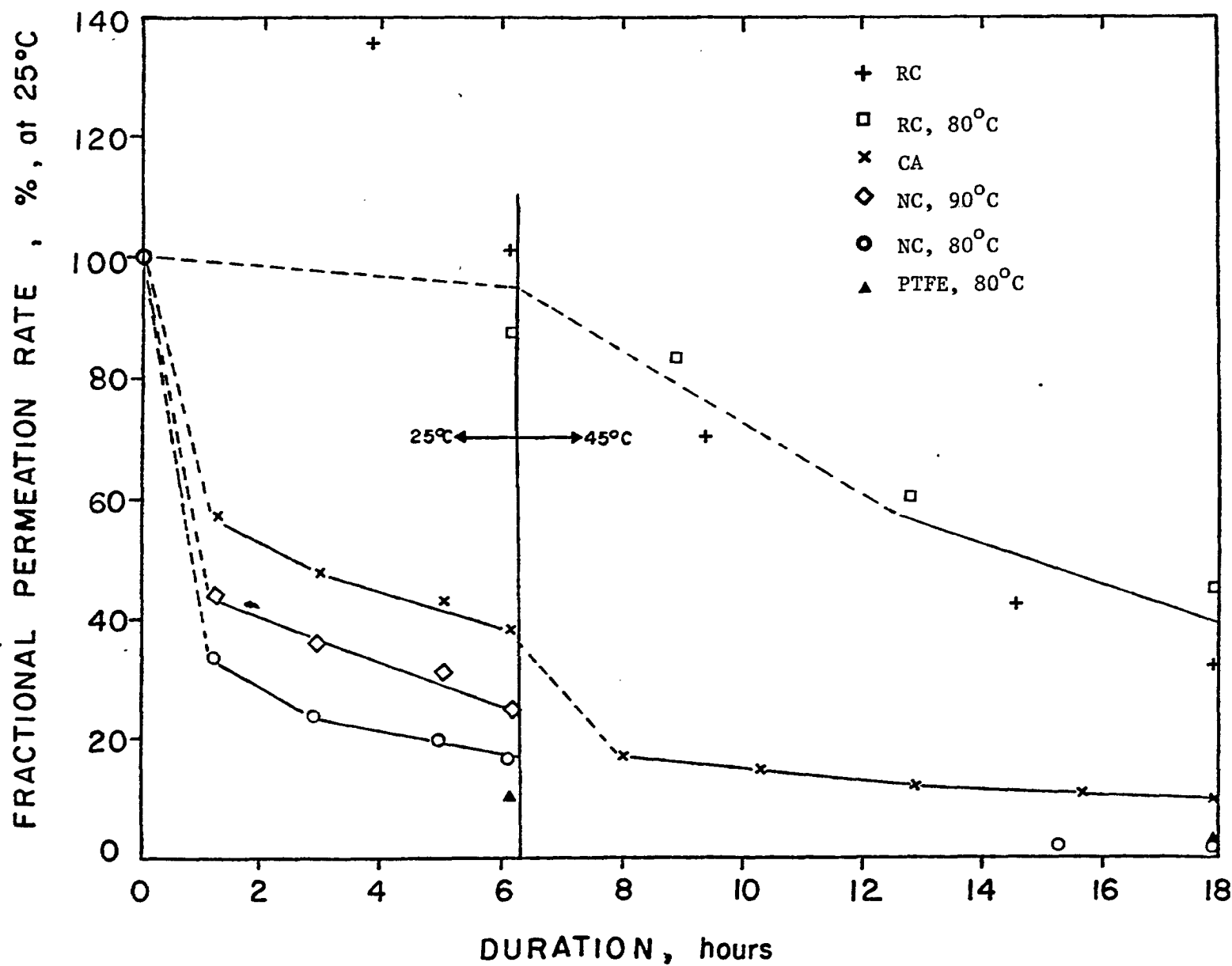
- a TDS was calculated as residue at 90°C
- b The minimum detectable limit for Ca is estimated to be 0.07 ppm.  
The corresponding limit for hardness as CaCO<sub>3</sub> is 0.175 ppm.
- c The minimum detectable limit for Mg is estimated to be 0.152 ppm.
- d The minimum detectable limit for Fe is estimated to be 0.118 ppm.
- f Analysis by ICP on fused ash.
- e Approximately 4% bitumen.







VARIATION of PERMEATION RATE with RUN DURATION



PERMEATE

Fig. 3.

BITUMEN  
(RAW EMULSION)

% T

4000                      3000                      2000                      1500                      800

