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AN EVALUATION OF THE USE OF POROUS MEMBRANES FOR THE
DEWATERING OF WELLHEAD BITUMEN/WATER/MINERAL EMULSIONS

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JUNE 1984

For submission to Separation Science and Technology

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
DIVISION REPORT ERP/ERL 84-17 (J)

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ABSTRACT

In situ bitumen and heavy oil recovery by steam stimulation can produce large volumes of oil-in-water emulsions. Several difficulties facing recovery operations are the limited water supply in relation to the volumes required for steam injection, and the processing of water-rich emulsions to low-water content bitumen. In current practice, these emulsions require substantial amounts of chemical additives with large settling tanks and elevated temperatures. An evaluation of the use of porous membranes for the treatment of these emulsions has been made which has led to the development of a process that will produce single pass (80%) steam quality water as membrane permeate and a bitumen-rich stream which can be processed by existing dewatering methods. Details of the performance of several membranes of various pore sizes are given and a comparison is made with existing single-pass steam boiler requirements. Of those tested, cellulose membranes resisted fouling by the bitumen thus were the most promising.

RESUME

La récupération in situ du bitume et huile lourde par stimulation par injection de vapeur d'eau produit une grande quantité d'émulsion (huile dans l'eau). Parmi les difficultés lors des opérations de récupération, on retrouve la quantité limitée d'eau comparé à la quantité requise pour l'injection de vapeur ainsi que le traitement de l'émulsion enrichie en eau pour produire une émulsion riche en bitume. En réalité, la présence de ces émulsions requiert l'utilisation de grandes quantités de produits chimiques et réservoirs de sédimentation à des températures élevées. On a considéré dans cette étude, l'utilisation de membranes poreuses pour le traitement de ces émulsions. Ceci nous a conduit au développement d'un procédé qui peut produire en une seule passe une qualité d'eau à 80% vapeur et constituée d'un perméat et d'une autre phase enrichie en bitume qui peut être traitée par des méthodes d'assèchement. On a étudié le rendement de plusieurs membranes de taille des pores différente ainsi que la comparaison des spécifications pour la chaudière à vapeur. Les membranes de cellulose résistent à l'encrassement par le bitume et apparaissent les plus prometteuses dans ce genre d'étude.

INTRODUCTION

Several in situ recovery operations for bitumen and heavy oil generate large amounts of stable oil-in-water (O/W) emulsions. This causes severe processing difficulties in subsequent treatment. A related problem is the amount of water required for steam generation, which may become a limiting factor for the exploitation of some deposits (1,2). Existing specialized steam generation facilities for recycling produced water to injection steam account for only a small amount of enhanced oil recovery (EOR) and in situ recovery steam supply (3,4,5). This can be attributed to the difficulty in producing suitable quality water from produced water, even for 80% steam generation.

The effects of clay, salts, minerals, dissolved species, and the nature of the bitumen/heavy oil have led to unusually high emulsion stability which interferes with processing. Current operations use large amounts of chemical demulsifiers that cannot be recovered, and elevated temperatures and pressures requiring external energy sources and costly facilities. The effect of clay on stabilizing O/W emulsions of Athabasca bitumen has been studied by Gewers (6). He reports a narrow range of pH in which this effect is minimized. The density difference between water and bitumen is small and causes difficulties in industrial separations. Since any bitumen-rich phase is likely to be a (W/O) emulsion, the density difference during a skimming type separation will be less than that of the isolated phases. As well, Broughman (7) reports the density of water-free bitumen and water overlap at 35°C and 115°C which further complicates the use of density differences for separation. These difficulties must be overcome for a satisfactory separation process and large volumes of emulsion must be processed on a continuous basis.

The use of porous membranes for breaking O/W emulsions is not unique. Trade literature as well as scientific literature are available in the public domain (8,9,10,11). However, this literature considers processing of highly refined petroleum fractions and seed oil emulsions, and do not include field generated bitumen and heavy oil O/W emulsions, containing clay, salts, minerals, and naturally occurring surfactants.

The work reported here was performed with untreated wellhead bitumen/water/mineral emulsions from a steam drive pilot recovery in the Athabasca tar sands deposit at Fort McMurray, Alberta. Currently, this emulsion is treated by the use of demulsifiers at elevated temperatures. Several different membrane materials and porosities have been considered with the goal of concentrating the bitumen and producing water of sufficient quality for 80% steam generators.

EXPERIMENTAL

A continuous flow system assembled for the simultaneous evaluation of the performance of six membranes is shown schematically in Fig. 1. When operating with the O/W emulsions "slugs" of bitumen in the circulation side of the membranes caused fluctuations in the operating pressure by interfering with the back pressure control valve. These were relatively minor fluctuations and were ignored. As well, the opaqueness of the emulsion precluded the use of the rotameter shown in Fig. 1, hence it was removed from the system. The flowrate was then measured volumetrically by collecting the outlet stream for a known period of time. A variable volume stroke reciprocating pump circulated the feed solution through the system. As with the back pressure control valve, bitumen slugs interfered with the action of the check valves. This effect was also minor and was overcome by increasing the pump's stroke volume to maintain the flowrate as measured at the outlet of the system.

The system operated at 1800 kPa for all of the experiments. The temperature of the feed solution was varied from 24°C to 45°C as described in the experimental results. The feed was circulated at 0.5 L/min, and the pressure drop for the six membrane holders was less than 30 kPa. A preliminary series of characterization experiments was performed to determine the pure water permeation rate (PWP) for each membrane. These were followed by potassium salt (KI) solutions, and the product permeation rate (PR) and the concentration of KI in the feed and permeates were determined. A function to describe the separation of KI is defined as:

$$f = \frac{\text{Reservoir concentration} - \text{Permeate concentration}}{\text{Reservoir concentration}} \quad (1)$$

where f is defined as the solute separation, and is reported as a per cent.

These experiments were followed by the emulsion experiments, without modification to the membranes. The KI solution in the reservoir and throughout the system was replaced by the O/W emulsion. The volume of the feed solution was 2 L which included the system's internal volumes. In the first case, 24°C was chosen as the operating temperature. The permeate was collected for various time durations, the PR determined, and the permeate was analyzed for total dissolved solids (TDS), metals (Mg, Ca, Fe), pH, silica (SiO₂), and total organic carbon (TOC). This experiment ran for 6 h during which various samples were collected for each membrane. Upon completion of the 6 h, the feed was replaced with a fresh emulsion sample and the temperature was increased to 45°C. Again, the permeate was collected for various time durations and analyzed as before. This experiment was carried out for a 6 h-period, interrupted overnight, and continued for another 6 h for a total of 12 h. Samples were collected as their volumes reached convenient levels for analysis.

RESULTS AND DISCUSSION

The membranes are shown in Table 1 along with the results of the KI solution experiments. This information is required to characterize the membranes' performance. The degree of KI separation is considered to be inversely proportional to the membrane pore size. Accordingly, the cellulose acetate (CA) membrane had the smallest pore size and the nitrocellulose (NC) and polytetrafluoroethylene (PTFE) membranes had the largest pore sizes. In general, heat treatment reduces the pore sizes of polymeric membranes by causing a relaxation of their structure by exceeding glass transition temperatures. A wide range of pore sizes was made available to evaluate the membranes' ability to remove dissolved species from the permeate. While the separation of dissolved components may be greater for smaller pore sizes, it is at the expense of reduced permeation rates. However, this is mitigated by the number and range of pore sizes on the membrane surface which are properties of the membrane material, fabrication method, polymer morphology, and molecular weight.

The results of the emulsion experiments are shown in Fig. 2 for the permeation rates and in Table 2 for the compositional analyses. The variation of the permeation rates show large excursions from their pure water permeation. This decrease of permeation appears to be caused by breaking the bitumen/water/mineral emulsion on the membrane surface along with the attendant fouling of the membrane by the bitumen. The exception to this behaviour is the regenerated cellulose (RC) membranes. While a slight decrease of permeation rate was observed for the two RC membranes during the 25°C operation, 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 (12,13). However, operation at 45°C caused a large decrease in permeation rate for all of the membranes. This indicates that operating at this temperature is not desirable for the long term use of these types of membranes.

In general, the appearance of the permeates was clear with varying degrees of amber colour, roughly inversely proportional to the membrane's KI separation. There was no evidence of sediment in the permeate even on long standing, although there was visible long term biological activity. As well, the permeate supported a large foam formation when it was shaken.

In Table 2, the various component analyses are compared with the original emulsion and with the limits for 80% steam generation for single-pass boilers similar to those available in the Athabasca bitumen field. In all cases at 24°C, the TDS of the permeates surpasses the standards required for the single-pass boilers. However, the PIFE membrane exhibited unusual two-phase permeation for the 45°C operation and demulsified bitumen droplets of 2 to 3 mm diameter could be observed in the permeate. These phenomena could be the result of the large pore size of the membrane combined with the strong preferential sorption of the bitumen onto the PIFE surface.

Analysis of the permeates for the concentration of selected metals is also reported in Table 2. Calcium and magnesium content exceeded the single-pass boiler requirement as did the calculated hardness. For iron (Fe) the analysis limit for inductive ion coupled plasma (ICP) used in this work is 0.118 ppm, which exceeds the single-pass boiler limit. Although the exact concentration of iron is not known, it is at least in the same range as the single-pass boiler limit, and assumed to have met the requirement. Only the SiO_2 (detected as Si) presented difficulties. The CA membrane's porosity was sufficiently small to meet the required concentration, but the other membranes were able to bring the silica content down to the range of the 80% steam generator's requirement. It is felt that further reduction of the membranes pore sizes will yield permeates that will meet the requirements.

To confirm that the organic material of the permeate was not bitumen (PTFE at 45°C excluded), attempts were made to extract the permeate with toluene. There was no evidence of the transfer of coloured material to the organic phase, nor was there any visible residue left by the evaporation of the toluene phase. To further evaluate the organic components, infrared analysis of the ethyl acetate extract of the acidified permeate was compared with the toluene extract of the original emulsion. The ethyl acetate extract showed the presence of many ester, acid, and other polar groups while the toluene extract of the bitumen showed mainly saturated hydrocarbon structures as well as some polar groups.

An unexpected phenomenon was the separation of the emulsion in the reservoir to form bitumen-rich and water-rich layers. The bitumen-rich layer floated on the surface, but sank when forced below the surface. This layer was retrieved and analyzed for water content by Dean and Stark analysis. The bitumen content was 23% at 25°C and 35% at 45°C. Since this effect was not anticipated, the retrieval of the bitumen-rich layer may have incorporated the water-rich emulsion. The rate of accumulation of this bitumen-rich phase was not determined. The remaining O/W emulsion in the reservoir continued to destabilize into two phases, with the black bitumen visible at the bottom and the water phase on top, muddy brown in colour and with visible particles. The original wellhead emulsion used as the feed for this work remained stable during the same period.

On the basis of the above observations, it is considered that the permeate contained a substantial amount of a naturally occurring stabilizing agent for the bitumen/water/mineral emulsion and its removal caused a separation of the emulsion into bitumen- and water-rich phases. This effect has been discussed by Gewers (6) where he describes the increases in stability of Athabasca bitumen in water emulsion, enhanced by the presence of asphaltenes and other polar material. This behaviour can be exploited to develop a membrane process capable of producing a permeate stream of high quality water for steam injection, a bitumen-rich stream for further processing by conventional means, and a water-rich stream for recycle to the membrane process and clay/mineral removal. This process would be installed to treat O/W emulsions, presumably at the wellhead, possibly as shown in Fig. 3. Because of the large variation of O/W emulsion properties and steam generation requirements, modifications of the pore sizes and operating conditions may be necessary for other regions and deposits, and could include the addition of chemical demulsifiers. Further recycle of the water and clay stream can be considered since it may contain recoverable bitumen, and is also a source of water for steam generation.

CONCLUSIONS

Porous membranes are capable of treating bitumen/water/mineral emulsions produced by in situ recovery of bitumen such as those found in the Athabasca deposit. An associated difficulty caused by the emulsion is membrane fouling by the bitumen, although regenerated cellulose membranes do not foul to the same extent as the other membrane materials studied here. Depending upon the end use of the permeate water, the membrane pore sizes can be adjusted to obtain the desired quality, and several ranges have been identified. A benefit of using the porous membranes described is the destabilization of the O/W emulsion to produce a bitumen-rich emulsion which would aid further processing. This effect appears to be related to the selective removal of polar material by the permeate.

ACKNOWLEDGEMENT

The authors wish to acknowledge the aid of A. Martineau of CANMET for the ICP analyses, M. Curtin of the University of Waterloo for the TDS and infrared analyses, and T. Matsuura of NRC Canada for the TOC analyses. The authors also wish to acknowledge the technical assistance of C. Nader of the University of Ottawa.

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Table 1 - Membrane Performance at 1800 kPa and 24°C with dilute KI solution

MEMBRANCE NO.:	1	2	3	4	5	6
Material ^a	NC	PTFE	RC	NC	RC	CA
Pore size, $m \times 10^{10}$	100	200	50	50	50	<u> </u> ^b
Supplier	Sartorius	Sand S	Sand S	Sand S	Sand S	CANMET
Heat treatment, °C x 10 min	80°C	80°C	<u> </u> ^e	90°C	80°C	<u> </u> ^e
(PWP) ^f , avg. g/h	63.43	27.75	5.14	49.18	4.86	38.57
(PR) ^{f, g} , g/h	63.09	24.94	5.35	50.15	5.04	37.94
F ^g , %	7.3	7	12	12	20	32

^aNC = nitrocellulose; PTFE = polytetrafluoroethylene;
RC = regenerated cellulose; CA = cellulose acetate

^b undetermined

^cS and S = Schleicher and Schuell

^dCANMET (fabricated in-house)

^e no heat treatment applied

^f surface area of $1.26 \times 10^{-3} m^2$

^g calculated separation for a feed of 2050 ppm KI

Table 2 - Analysis of Permeate for the membranes

MEMBRANE NO.:	1	2	3	4	5	6	Original emulsion	80% Steam Requirement
Material/ heat treatment	NC/ 80°C	PTFE/ 80°C	RC	NC/ 90°C	RC/ 80°C	CA		-
24°C Run								
TDS, ppm ^a	635	740	506	738	661	371	55,000 ⁱ	8,000
Ca, ppm ^b	<0.07	-	<0.07	<0.07	<0.07	< 0.07	1.8	-
Mg, ppm ^c	<0.15	-	<0.15	<0.15	<0.15	< 0.15	0.45	-
Fe, ppm ^d	<0.12	-	<0.12	<0.12	<0.12	< 0.12	4.7	0.05
SiO ₂ , ppm	63.3	-	59.8	63.2	56.6	39.4	157	50
Suspended solids	no	no	no	no	no	no	yes	0 mg/L
Suspended oil	no	no	no	no	no	no	yes	1.0mg/L
pH	7	7	7	7	7	7	7	-
Total hardness as CaCO ₃ , ppm ^b	0.18	-	0.18	0.18	0.18	0.18	4.6	0.5
TOC, ppm of C	45.6	76.8	81.4	69.0	65.0	48.3	-g	-
45°C Run								
TDS, ppm ^a	431	NA	771	-	755	173	55,000	8,000
Ca, ppm ^b	<0.07	1.62	<0.07	-	<0.07	<0.07	1.8	-
Mg, ppm ^c	<0.15	0.52	<0.15	-	0.17	<0.15	0.45	-
Fe, ppm ^d	<0.12	2.75	<0.12	-	<0.12	<0.12	4.7	0.05
SiO ₂ , ppm	59.6	85.3	54.9	-	58.2	26.4	157	50
Suspended Solids	no	-	no	-	no	no	yes	0 mg/L
Suspended oil	no	visible	no	-	-	no	yes	1.0 mg/L
pH	7	7	7	-	7	7	7	-
Total hardness as CaCO ₃ , ppm ^b	<0.18	4.1	<0.18	-	<0.18	<0.18	4.6	0.5
TOC, ppm of C	50.1	-	63.9	-	61.3	35.5	-g	-

^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 CaCO₃ 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.

^e Analysis by ICP on fused ash.

^f Approximately 4% bitumen.

^g from Fulton, (1982)

^h 1,000 to 1,500 ppm as ash

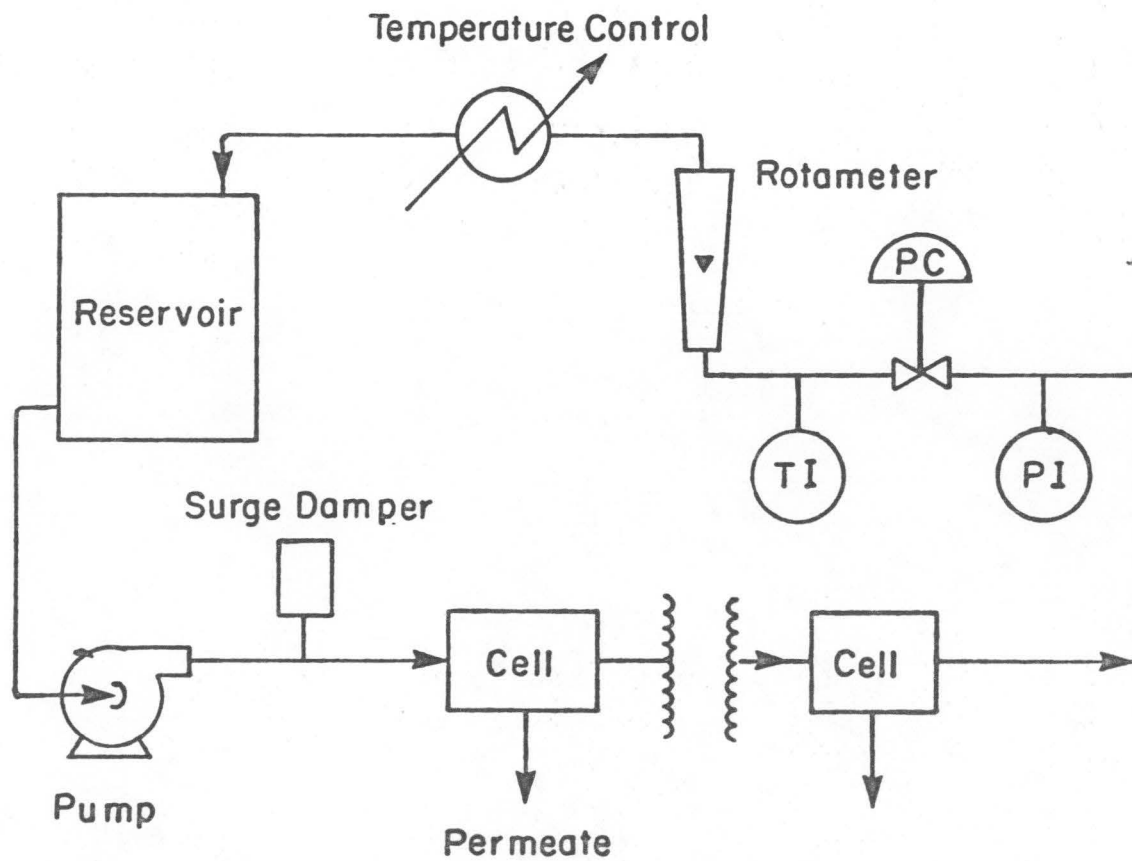


Fig. 1 - Continuous system for the evaluation of membrane performance.

VARIATION of PERMEATION RATE with RUN DURATION

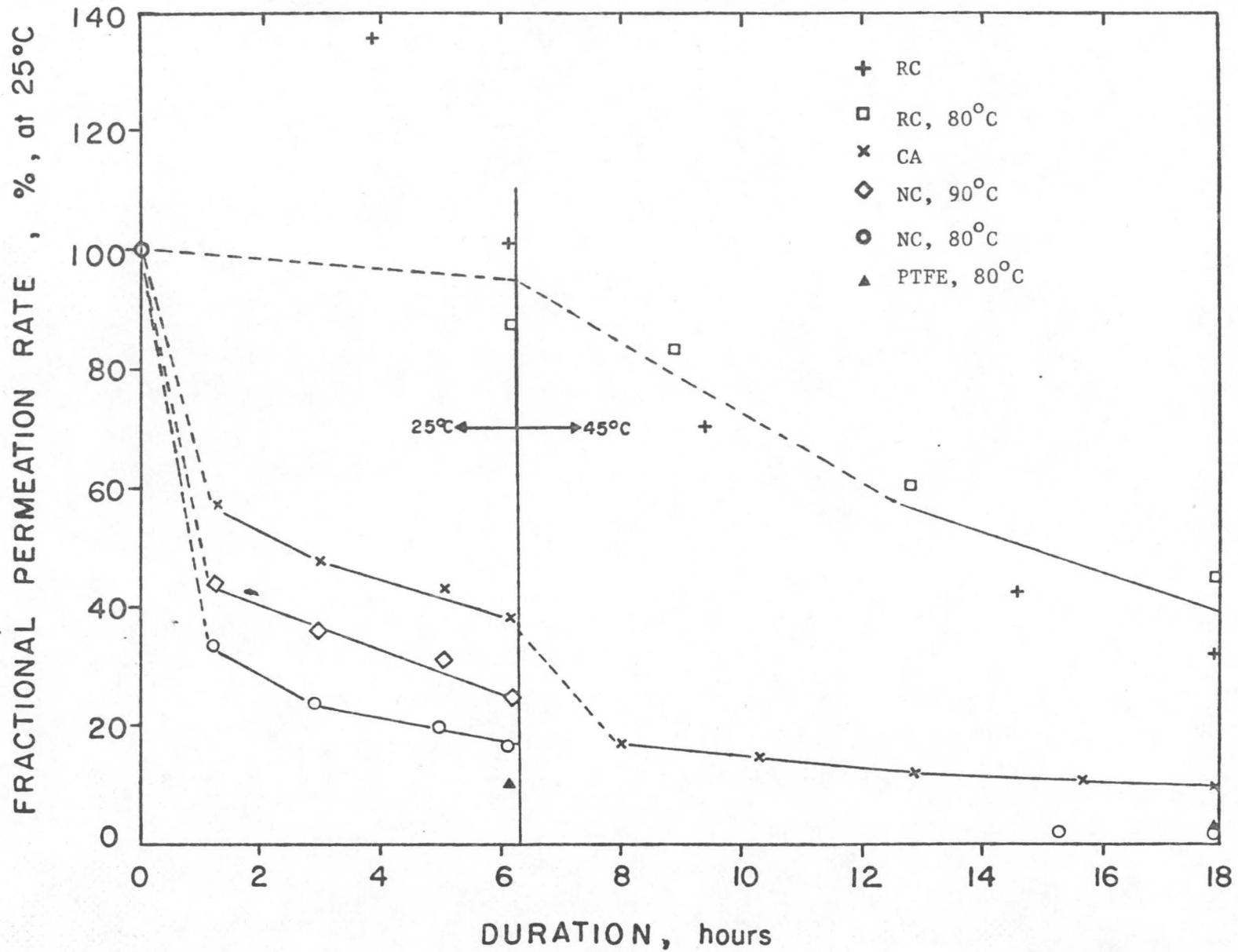


Fig. 2 - Variation of permeation rate with run duration.

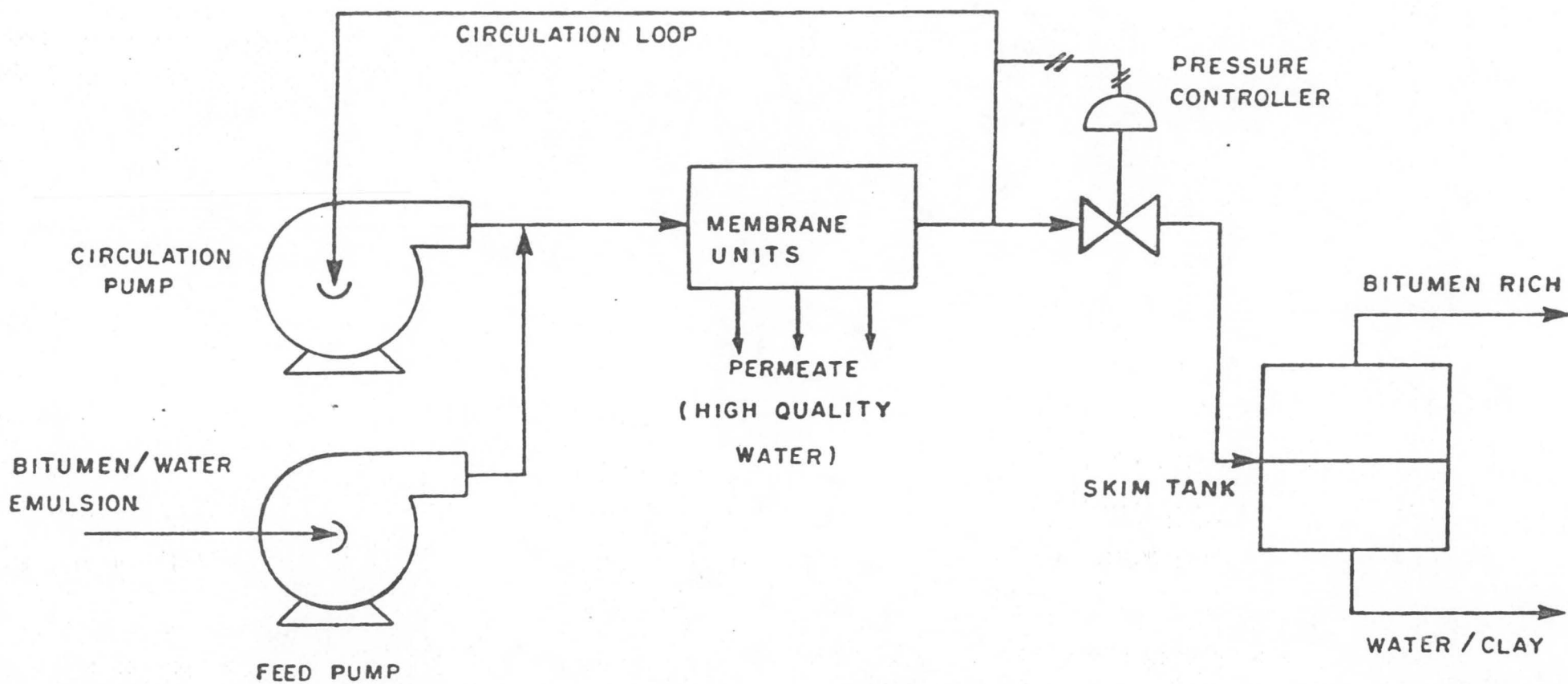


FIG. 3 Process configuration for the selective removal of stabilizing components from bitumen/water emulsions by porous membranes