Ultrafiltration of Oil Field Produced Water for Oil Removal

by
Thomas A. Krug (Zenon Environmental Inc., Burlington, Ontario)
Brian Farnand (Energy, Mines and Resources, CANMET/ERL, Ottawa, Ontario)

Abstract

Cross flow ultrafiltration systems which have been successfully applied to the treatment of emulsified oils in many industries and may provide a valuable alternative to conventional treatment of oil field produced water emulsions. Experiments were conducted using a variety of 1/2" tubular ultrafiltration membranes to treat produced water from a number of different sites in Western Canada. The flux rates obtained with tubular membranes and samples from 3 of 9 sites tested were greater than 4.0 $m^3/m^2/d$ and stable for the duration of the tests (>5 days). The flux obtained with samples from other field locations varied greatly and some generated flux rates of 1-2 $m^3/m^2/d$. Ongoing work has been focused at improving the flux for sites where initial values were low. Preliminary results have suggested that a 56% increase in flux can be obtained with an improved membrane and a further 32% improvement can be obtained by a small alteration in the chemistry of the produced water.

Introduction and Background

Enhanced oil recovery operations in Western Canada and elsewhere often employ steam stimulation to enhance oil recoveries from formations containing heavy oil. These steam stimulation processes require large volumes of water for steam generation and injection into the formation and generate large volumes of produced water contaminated with oil and other material. Since many recovery operations in Western Canada are located in water short or environmentally sensitive areas, effort has been directed in recent years to developing efficient and economic processes for the recycling of the produced water for treatment and reuse as boiler feedwater.

Several enhanced oil recovery (EOR) operations are currently recycling some portion of their produced water using various combinations of conventional treatment. Oil field boiler water requirements dictate that all oil, suspended solids, and hardness must be removed and frequently silica levels must also be reduced. Some sites where highly saline produced water is generated also require reduction of dissolved solids. The presence of natural or added surfactant material in many produced waters results in very stable oil in water emulsions. The treatment of this produced water at some sites by conventional methods can be difficult as a result of these highly stable emulsions.

The produced fluid from the wellhead contains oil and between 2 and 10 barrels of water per barrel of oil. Some of this water may be present in the oil as a water in oil emulsion while the balance may be a distinct produced water phase containing emulsified oil. The produced fluid is generally treated in a free water knock out (FWKO) tank and high temperature separator (HTS) to separate as much of the oil and water as possible. Water from the FWKO and HTS is generally combined and sent to a skim tank where some residual oil may be removed and recycled back to the recovery process. This water is often disposed of by deep well injection or is sent to further treatment for recycle.

If the water is to be recycled, as shown in Figure 1, the effluent from the skim tank is usually treated in an induced gas flotation (IGF) unit and sand filter for the removal of suspended solids and oil. Considerable quantities of chemicals must be added to maintain the performance of these units. Once oil and solids are removed the water is sent to a warm lime softening process for hardness and silica reduction then to ion exchange for removal of residual hardness before being recycled to the boiler.

Problems can be encountered with conventional treatment processes which can be expensive and difficult to operate as a result of the chemicals required and the large number of unit operations. The

ideal produced water treatment process would have a simplified flow scheme and would require fewer chemicals.

Cross flow ultrafiltration (UF) processes have been accepted as efficient and economical methods of treating many industrial waste streams containing emulsified oils including cutting oil emulsions. Since UF is a cross flow filter system it can handle higher oil levels than a sand filter thus eliminating the need for the IGF and some of the functions of the skim tank. The UF also provides a absolute barrier smaller than is possible with sand filters resulting in a higher quality filtrate and elimination of oil breakthrough during upset conditions. Figure 2 shows how the UF process might fit into the overall produced water treatment process.

This work involves an examination of the potential of using an ultrafiltration process to remove emulsified oils from produced water to improve the efficiency of recycle operations.

Flat Sheet Membrane Testing

The initial testing work involved the use of small flat sheet NRC membrane test cells each with a 13 cm. diameter membrane area. Membranes of six different chemical compositions were examined initially. Produced water containing 1,700 mg/L of oil was obtained from the wellhead of an EOR operation at Ft. McMurray Alberta. The oil was present in the produced water in a very stable emulsion.

These tests identified two symetric membranes of polysulphone (PS) and CHP (proprietary formulation) and one assymetric thin film composite (TFC) membrane of an undetermined formulation as the optimal membranes. The two symetric membranes yielded flux rates of 0.8 and 1.1 m^3/m^2/day and the TFC membrane yielded a flux of 1.05 m^3/m^2/day after 20 hours of operation and concentration of the original feed by a factor of 1.25.

All three membranes removed all suspended oil and solids and reduced levels of dissolved organic and solids. The TFC membrane constently produced a higher quality permeate than the two other membranes. From an initial feed containing 2,050 mg/L of total organic carbon (TOC) and 990 mg/L of total dissolved solids (TDS) the symetric CHP and PS membranes generated permeate containing 47 to 58 mg/L of TOC and 380 - 400 mg/L TDS. The TFC membrane generated a permeate containing 28 mg/L of TOC and 261 mg/L of TDS.

A batch concentration test was also conducted with the PS, CHP, and TFC membranes to determine the effect on membrane performance of concentration of the original feed by a factor of 10. The flux for the three membranes declined during the initial 17 hours of concentration to a concentration factor (CF) of 1.43 but remained relatively stable at 0.5 m^3/m^2/day for the PS & CHP membranes and at about 0.4 m^3/m^2/day for the TFC membrane during the remainder of the concentration test.

These initial tests demonstrated the technical feasibility of using ultrafiltration for the treatment of produced water oil emulsions but it was recognized that higher flux rates would be necessary for economic operation.

Configured Membrane Testing with Ft. McMurray Wellhead Produced Water

Following the initial flat sheet tests, experiments were conducted using a membrane test unit consisting of 6, one foot long 1/2" diameter tubular membranes. The performance of this test module can be used to more accurately predict the performance of larger systems since a full scale membrane system would consist of a bank of these half inch tubular membranes.

Initial testing with this tubular membrane module using the same CHP membrane and the same produced water as was used in the flat sheet test obtained a flux rate of 5.0 m^3/m^2/day, a full order of magnitude greater that that obtained using the flat sheet configuration. The difference in performance is believed to be a result of different levels of turbulence in the two systems. The Reynolds number in the flat sheet test cell was estimated to be between 500-600 while the Reynolds

number in the tube was estimated at over 30,000. The high level of turbulence in the tube is considered to be sufficient to prevent the buildup of gel layer which reduces the flux rate in the less turbulent system.

Tests were conducted using fresh sample of the Ft. McMurray wellhead produced water and 6 different tubular membranes. The membrane materials tested included a polyethersulphone (PES), a polyvinyldifluoride (PVDF), a polyolefin (PO), two CHP membranes, and second proprietary membrane referred to as HPC.

Figure 3 shows the flux rates obtained over the duration of the test using the CHP-TFC membrane. The raw feed was concentrated during the first few hours of operation by a factor of 10. The permeate was recycled back to the process tank and the system was operated in this mode for over 200 hours. The flux rate throughout the entire test remained stable at approximately 5 m^3/m^2/day (125 U.S.gallons/ft^2/day or gfd). The permeate generated with this membrane had some residual colour (187 alpha units) and TOC (70 mg/L) but all suspended oil and solids were removed and considerable (>50%) reduction in hardness was achieved. Table 1 shows the flux and permeate quality obtained with all membranes tested.

The results of these tests demonstrated that high and stable flux rates could be obtained with a number of membranes in a 1/2" tubular configuration using produced water containing 1,000 mg/L of heavy oil concentrated by a factor of ten. The CHP-TFC membrane was selected for further testing as a result of its very stable flux rate and high quality permeate.

Configured Membrane Testing With Different Produced Waters

A series of thirteen experiments were conducted with samples of produced waters from 8 different EOR sites to determine if the high and stable flux rates obtained with the produced water sample from the Ft. McMurray area could be obtained with other samples as well. Oil industry representatives had expressed an interest in treating produced water which had been processed through their FWKO and HTS and some samples for these tests were obtained from these points in the process rather than directly from the wellhead.

In general, the procedure for the tests involved concentrating the raw feed by a factor of 10 then operating in a recycle mode for a period of one to two weeks. Cleaning of the membranes was conducted as necessary to maintain the flux rates at high levels.

The results of the tests demonstrated that the performance of the membrane system is highly site specific and fluxes ranged between 1.0 m^3/m^2/day and over 4.0 m^3/m^2/day with samples from different EOR sites. Samples from two of the sites obtained fluxes as high as that obtained previously with the original Ft. McMurray sample indicating that little membrane fouling was occurring. The oil emulsions remained stable throughout these tests.

The characteristics of the flux data for three of the sites were typical of systems where the flux is controlled by a gel layer on the surface of the membrane. The fluxes for these samples were between 1 and 2 m^3/m^2/day but were stable at these levels. In some cases, free oil was removed from the process tank during the experiments suggesting that the elevated temperature, the concentration, and some aeration caused the emulsion to break. It is believed that the free oil in the destabilized emulsion resulted in a gel layer on the membrane surface and low flux rates. The fact that the emulsion breaks upon concentration may be used to advantage by concentrating only to the point where the emulsion breaks then using simple gravity separation to remove oil .

Three of the emulsion sites tested showed fluxes not as high as were obtained with the Ft. McMurray emulsion but higher than the 1 - 2 m^3/m^2/day flux rates obtained for some other samples. These tests were characteristic of systems where some gel layer was formed on the membrane but this gel layer was not as severe as in other tests. During these tests the emulsions remained stable.

These tests demonstrated that high flux rates and high quality permeate could be obtained treating produced water samples and that the performance is not related to the level of oil in the produced

water as much as it is to the stability of the emulsion present. The flux rates obtained with different samples of produced water varied greatly and improvements in flux will likely be required to make the technology competitive against conventional treatment for some EOR sites.

Improvements in system performance may be obtained in a number of different ways including optimizing the membrane pore size and chemistry and the operating strategies used to process the produced water. Ongoing membrane development for other oily water applications had suggested that improvements in system performance could be obtained with membranes recently developed which have been shown to produce higher fluxes and possibly more resistance to fouling. The overall flux will also be improved by operating the process in a batch rather than feed and bleed mode. The design flux for a full system will be the average of the high flux rate obtained initially and the lower flux rate obtained at the end of processing the batch. Cleaning would return the flux rate to its high level at the start of the subsequent batch.

In some situations it may be necessary to concentrate only a small amount to induce the emulsion to break and have the remaining oil removed by conventional means. It may also be possible to improve system performance by changing the emulsion chemistry through the addition of inexpensive additives.

Ongoing Work on Process Optimization

Several of the operating strategies identified for improving system performance are being examined in ongoing work. More detailed emulsion characterization work is also being conducted to identify characteristicts which can be used to predict emulsion stability and membrane performance.

An addition sample of produced water was obtained from an EOR site where previously the flux had been only about 1.0 m^3/m^2/day. In the first test with this sample a flux of approximately 1.8 m^3/m^2/day was obtained with the FLT-C membrane which is similar to the CHP-TFC previously tested while a new HLT-C membrane obtained a flux of 2.9 m^3/m^2/day at an operating pressure of 100 psi. The permeate quality with the HLT-C was slightly lower than for the FLT-C (250 alpha units of colour vs. 150 alpha units) but it is expected that when more complete analytical results are available, they will show both permeate qualities to be acceptable. In the second test the pH of a portion of the same sample was increased from 7.5 to 9.0 with NaOH to stabilize the oil emulsion present. This adjusted pH resulted in an improvement in the flux rate for the HLT-C membrane up to 3.5 m^3/m^2/day at 100 psi but there was no significant change in the flux rate for the FLT-C membrane. Preliminary results for these tests are shown in Table 2.

The results of these tests have demonstrated that significant improvements in flux rate can be obtained with a newly developed HLT-C membrane and by altering the chemistry of the feed.

Conclusion

The results of this work have demonstrated the potential of using a cross flow tubular ultrafiltration system to remove oil from produced water at enhanced oil recovery operations. The performance of the membrane system is highly site specific and appears more related to the stability of the emulsified oil rather than the absolute amount of oil present. Samples from 3 of 9 sites tested maintained high stable flux rates above 4 m^3/m^2/day and showed no signs of membrane fouling. Other samples tested obtained flux rates as low as 1 m^3/m^2/day and showed signs of membrane fouling.

Methods of improving overall system performance at sites where low flux rates were obtained are currently under investigation. Preliminary results have demonstrated that a 56% increase in flux can be obtained with an improved membrane and a further 32% improvement can be obtained by altering the chemistry of the produced water.

We believe the current work will demonstrate strategies which can be used to improve system performance sufficiently to increase the number of EOR sites where economic application of this technology is possible.

References

Zenon Environmental Inc. (1985) "Technical and Economic Assessment of the Application of Membrane Technology for Treating Oil / Water / Mineral Emulsions," Report Prepared for Energy Mines and Resources, CANMET / ERL, Contract # OSQ83-00203.

Zenon Environmental Inc. (1987) "Membrane Processing of Oil Field Produced Water for Enhanced Oil Recovery (EOR) Steam Generation," Report Prepared for Energy Mines and Resources, CANMET / ERL, Contract # O3SQ.23440-5-9111.

Acknowledgments

The authors wish to acknowledge the assistance of EMR CANMET / ERL for ongoing technical advice and providing funding for this work.

FIGURE 1
Conventional Produced Water Treatment Process

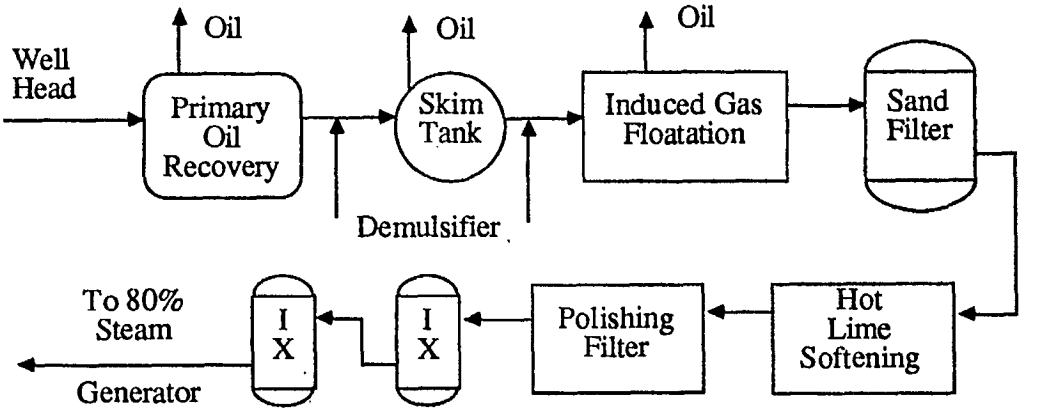

FIGURE 2
Potential Membrane Treatment Process

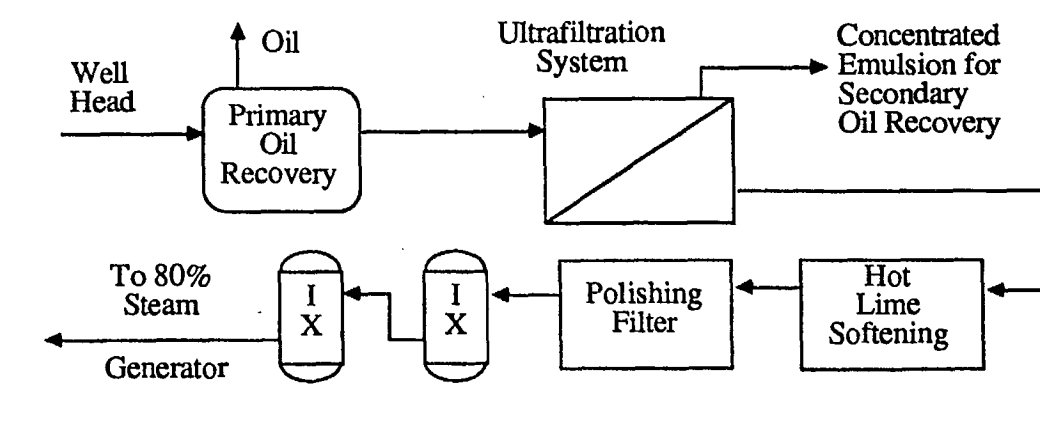

FIGURE 3

Flux for CHP-TFC Tubular Membrane With
Ft. McMurray Wellhead Sample

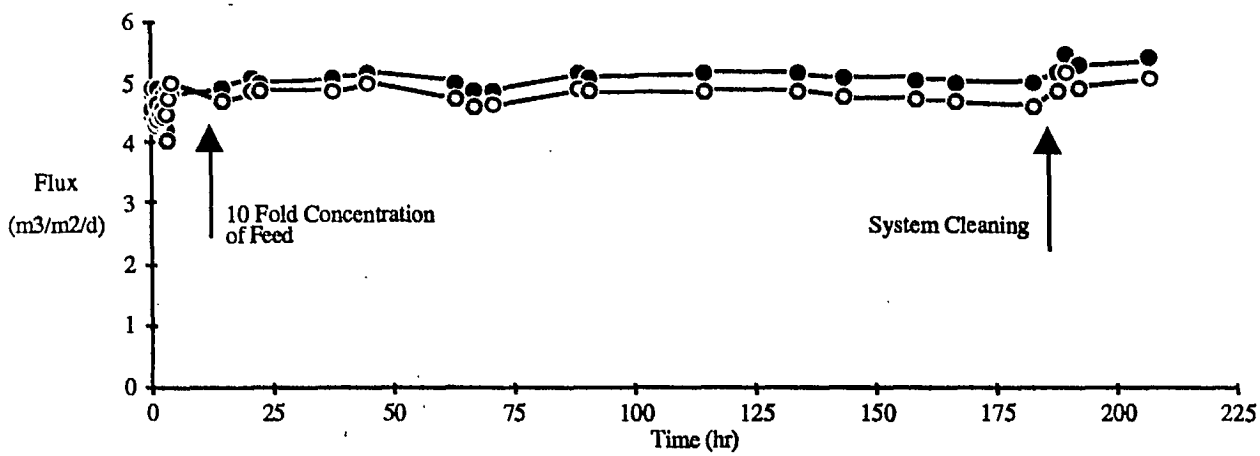

TABLE 1

Results for 1/2" Tubular Membranes with Ft. McMurray Wellhead Sample

	RATE (m3/m2/d)	COLOUR (alpha units)	TOC (mg/L)	HARDNESS (mg/L)
FEED	---	na	900	21
PERMEATE				
PS-A	8 - 4	520	180	10
PS-B	8 - 4	695	180	12
CHP-CA	8 - 6	1,400	215	15
CHP-TFC	4.9	187	70	8
HPC	7.0	1,500	205	12
PO-A	4.8	2,700	na	na

TABLE 2

Results for 1/2" Tubular FLT-C & HLT-C with Site "E" HTS Water Sample

MEMBRANE	FLUX (m3/m2/d)				PERMEATE COLOUR (alpha units)
	No Additive		Additive Used		
	100 psi.	50 psi.	100 psi.	50 psi.	
FLT-C	1.8	0.8	1.6	0.8	150
HLT-C	2.9	1.8	3.5	2.5	250