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DEVELOPMENT OF A MEMBRANE-BASED PROCESS FOR THE TREATMENT OF OILY WASTE WATERS

Contract No. DE-AC22-92MT92005

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Program Manager: Scott B. McCray
Principal Investigator: Scott B. McCray
Technical Project Officer (COR): Gene Pauling
Reporting Period: December 5, 1992, to March 4, 1993

from
Bend Research, Inc.
64550 Research Road
Bend, Oregon 97701-8599

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EXECUTIVE SUMMARY

This is the fourth quarterly report from Bend Research, Inc., (BRI) to the U.S. Department of Energy (DOE) for work performed under Contract No. DE-AC22-92MT92005, titled "Development of a Membrane-Based Process for the Treatment of Oily Waste Waters." This report covers the period from December 5, 1992, to March 4, 1993.

The overall goal of this program is to develop a system based on reverse osmosis (RO) membranes that can treat oily water economically. This system will be based on the use of thin-film-composite (TFC) membranes that consist of a selective coating placed on a solvent-resistant hollow-fiber support. For this program, we plan to develop solvent-resistant hollow-fiber supports and coat them with a "loose RO" coating. We developed the coating, which is designated TTM, in previous work for the treatment of oily waste waters.

During this reporting period, work was focused on

- 1) fabrication and testing of large-scale hollow-fiber modules,
- 2) performing preliminary field tests using these modules, and
- 3) arranging for a demonstration test of this technology. Our results show that the solvent-resistant TTM hollow-fiber modules perform well when operated on oily waters.

During the next reporting period, we plan to complete arrangements for the demonstration test of this technology. This field test, preparation of the final report, and technology transfer are the only tasks remaining in this program.

I. INTRODUCTION

This is the fourth quarterly report from Bend Research, Inc., (BRI) to the U.S. Department of Energy (DOE) for work performed under Contract No. DE-AC22-92MT92005, titled "Development of a Membrane-Based Process for the Treatment of Oily Waste Waters." The purpose of this program is to develop a system based on reverse-osmosis (RO) membranes that can treat oily water economically. This system will be based on the use of thin-film-composite (TFC) membranes that consist of a selective coating placed on a solvent-resistant hollow-fiber support. For this program, we plan to develop solvent-resistant hollow-fiber supports and coat them with a "loose RO" coating. We developed the coating, designated TTM, in previous work for the treatment of oily waste waters. This report covers the period from December 5, 1992, to March 4, 1993.

During this reporting period, work was focused on

- 1) fabrication and testing of large-scale hollow-fiber modules,
- 2) performing preliminary field tests using these modules, and
- 3) arranging for a demonstration test of this technology. Our results show that the solvent-resistant TTM hollow-fiber modules perform well when operated on oily waters.

II. PROJECT DESCRIPTION

This program is divided into seven tasks. A summary of the work to be performed in this program follows.

Task 1: Develop Hollow Fibers

Hollow-fiber supports will be made from high-strength, solvent-resistant polymers. These fibers will be physically robust and have 1) high permeability to assure high fluxes, and 2) smooth lumen (interior) surfaces to assure uniform coating of the hollow-fiber support with the permselective coating.

Task 2: Evaluate Hollow Fibers

The fibers made in Task 1 will be evaluated in a series of tests to ensure they are suitable for this application. These tests include 1) examining the texture of the lumen surface, 2) measuring the permeability of the fibers, 3) measuring the strength of the fibers, and 4) measuring the solvent resistance of the fibers.

Task 3: Make Small-Scale Modules

Small-scale hollow-fiber modules will be made using the fibers, and the lumens of the fibers will be coated with our loose-RO TTM coatings. The modules will be evaluated in standard tests to ensure the integrity of the coating.

Task 4: Test Small-Scale Modules

The small-scale modules made in Task 3 will be tested in the laboratory under controlled conditions. The modules will be evaluated on feed streams of oily waste waters obtained from various sources. Parametric and long-term tests will be conducted.

Task 5: Construct Large-Scale Modules

Large-scale modules will be constructed using standard module-preparation procedures developed at Bend Research. These

modules will be constructed for use in a demonstration unit to be provided by the contractor.

Task 6: Operate Demonstration Unit

The effectiveness of this technology will be demonstrated by operating the large-scale modules on actual oily waste waters. Field-test sites will be identified and prepared for the demonstration of this technology. A test plan will be developed before the demonstration is performed.

Task 7: Technology Transfer

Journal articles and conference and symposia presentations will be prepared. This technology will be transferred to the oil and gas industry and the scientific community.

III. PROJECT STATUS

In this section, a detailed description is presented of the work performed during this reporting period.

III.A. MAKE AND TEST LARGE-SCALE MODULES

The purpose of this work is to make and test large-scale modules using the fibers developed in this program. During this reporting period, we made modules containing 1 m² of membrane. These modules will be used in the demonstration test of this technology.

Once the modules were made, the lumen (inside) surfaces of the fibers were coated with the TTM coatings previously developed at BRI. To accomplish this, we used a semi-automatic coating apparatus available at AquaAir Environmental, Inc. (Bend, Oregon). This company, a spin-off of Bend Research, manufactures non-solvent-resistant hollow-fiber modules and membrane systems for environmental applications. The semi-automatic coating apparatus was previously developed at Bend Research for coating modules containing up to 8 m² of membrane area.

Table I shows the results of preliminary evaluations of these modules under our standard evaluation conditions. As these data show, these larger-scale modules perform as well as the small- and moderate-scale modules (i.e., modules containing 0.01 m² and 0.1 m² of membrane, respectively) made earlier in this program (see our quarterly reports dated October 20, 1992, and December 29, 1992).

The data in Table I also show the performance of the modules after cycling them to 200 psig for 400 to 900 cycles. These data show that the performance of Module Nos. SR-2 and SR-3 changed only slightly, demonstrating the robustness of these modules. However, the salt rejection of Module No. SR-1 declined. We believe this loss in salt rejection was caused by damage to the fibers during the modularization process. Based on these results, Module Nos. SR-2 and SR-3 will be used in the demonstration tests.

Table I. Performance of Large-Scale (1-m²) TTM-40 ModulesTest conditions: 100 psig, 25°C, 2000 ppm MgSO₄, pH 6

Module No.	Initial Test		After Pressure Cycling*	
	Water Flux (gal/ft ² -day)	MgSO ₄ Rejection (%)	Water Flux (gal/ft ² -day)	MgSO ₄ Rejection (%)
Target	>20	>85	--	--
SR-1	20	89	25	73
SR-2	38	93	31	88
SR-3	20	85	27	89
*Pressure-cycling conditions: 200 psig for 1 minute, 0 psig for 1 minute Modules SR-1 and SR-3 were cycled 900 times. Module SR-2 was cycled 400 times.				

III.B. PERFORM PRELIMINARY FIELD TESTS

Due to unforeseen problems in arranging for the demonstration test, we performed preliminary field tests of moderate-scale (0.1-m²) modules previously developed in this program (see our quarterly report dated December 29, 1992 for a description of these modules).

Three field tests were performed in this reporting period. In these tests, approximately 5 gallons of feed water was obtained. This feed solution was then fed to the membrane module using a small circulation pump, as shown in Figure 1. As "clean" permeate was removed from the feed solution (e.g., as recovery increased), the concentration of contaminants in the feed solution increased. Steps were taken during these tests to reduce or eliminate exposure of the feed stream to oxygen. Thus, these tests are realistic simulations of the operating conditions to which the membranes would be exposed in a continuous process.

Figure 1. Schematic of Test Loop Used During Preliminary Field Tests

Table II summarizes these preliminary field tests. In the first test, conducted on an off-shore platform near Santa Barbara, California, the modules produced a permeate containing 28 ppm oil and grease. This represented a rejection for oil and grease of 88%. Unfortunately, the flux through the membrane was only about 3 gal/ft²-day. We believe the reason for the low flux was the presence of additives that are used to improve the performance of the induced-gas-flotation unit used to treat the oily water.

As the data in Table II show, we obtained much better results in subsequent field tests. Figure 2 shows the water flux and concentration of oil and grease in the permeate as functions

Table II. Summary of Preliminary Field Tests

Test Site	Module Type	Feed Oil and Grease (ppm)	Permeate Oil and Grease (ppm)	Oil and Grease Rejection (%)	Water Flux (gal/ft ² -day)
Santa Barbara, California	TTM-40	250	28	88	3
Friendswood, Texas	TTM-20	350	5	98	22
Grand Isle, Louisiana	TTM-40	280	7	98	20

Figure 2. Performance of TTM-20 Hollow-Fiber Module During Preliminary Field Tests at Friendswood, Texas

Conditions: water from bottom of free-water knockout tank, 60-psig inlet pressure, 40°C

of recovery for a TTM-20 module operating on the feed solution from Friendswood, Texas. In this case, the module rejected more than 98% of oil and grease, producing a permeate that contained less than 10 ppm oil and grease at recoveries up to 99%. The data in Figure 2 also show that the TTM-20 module maintained a high flux--22 gal/ft²-day--during this test.

Similar results were obtained at Grand Isle, Louisiana, this time using a TTM-40 module. In those tests, the modules rejected more than 98% rejection of oil and grease, while maintaining high flux.

Based on these preliminary field tests, we are confident that this technology will work well in the demonstration test scheduled for the next reporting period.

III.C. OPERATE DEMONSTRATION UNIT

During this reporting period, our commercialization partner, AquaAir Environmental, Inc., (Bend, Oregon) shipped the demonstration unit to Friendswood, Texas, the site of the demonstration test. Figure 3 shows a schematic of this test

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Figure 3. Demonstration Unit

unit. Note that this test unit is designed to test technology currently under development by AquaAir, as well as the improved, solvent-resistant technology that is the focus of this program.

IV. PLANNED ACTIVITIES

During the next reporting period, we hope to perform the demonstration test of this technology. The demonstration test, preparation of the final report, and technology transfer are the only tasks remaining in this program.

V. SUMMARY

During this reporting period, we completed the fabrication and testing of large-scale hollow-fiber modules. In addition, we performed preliminary field tests using these modules at three test sites. The results of these tests show that this technology will be suitable for treating oily waste waters. Additionally, we have arranged for a demonstration test of this technology.

Report Distribution List

Three copies to: Document Control Center, U.S. Department of Energy

Pittsburgh Energy Technology Center, P.O. Box
10940, MS 921-118, Pittsburgh, PA 15236-0940

References: None.

Publications

No publications have been prepared on this technology. However, some of these results were presented verbally at the Energy Sources Technology Conference & Exhibition, which was held January 31 to February 4, 1993, in Houston, Texas.

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