July 1, 1993

FINAL STATUS REPORT - SUMMARY - RESEARCH

I. Development and Application of Aeration Technologies - Water 37

Program Managers: Heinz Stefan
John Gulliver
Michael Semmens
St. Anthony Falls Hydraulic Laboratory
Mississippi River at 3rd Avenue S.E.
University of Minnesota
Minneapolis, Minnesota 55414
612-627-4010

A. M.L. 91 Ch. 254 Sec. 14 Subd. 4(k) Appropriation: $148,000
Balance: $ 0

This appropriation is to the University of Minnesota, St. Anthony Falls Hydraulic Laboratory to study how to optimize membrane aeration and the hydraulic design of by-pass type aerator systems.

II. Narrative

Aeration technology is applied in hundreds of Minnesota lakes and reservoirs for at least three purposes: (a) to prevent winterkill of fish in shallow lakes under ice cover, (b) to reduce nutrient release rates from the sediments (c) in aquaculture to provide aerated water to high-density fish populations. The number of applications is on the increase. A major uncertainty in the design, selection and application of aeration systems is the often observed increase in oxygen demand after aeration systems are installed and operated. As a result, the improvement in dissolved oxygen is often less than anticipated, even zero. The study provides resource managers with information about installation of typical aerators (locations, orientations, etc.) under summer and winter conditions such as to minimize bottom interference and hence to maximize aeration efficiency and prevent failures (non-achievement of dissolved oxygen target).

A novel bubbleless hollow fiber membrane aerator is evaluated for the oxygenation of water. In this process pure oxygen is maintained on the inside of a bundle of dead-ended fibers at a pressure below the bubble point, and the water to be aerated is caused to flow over the outside of the fibers. Because pure oxygen is used, the oxygen diffuses across the porous fiber walls and dissolves quietly into the water without the formation of bubbles. The process provides 100% oxygen transfer efficiency at a reasonable power input.

III. Objectives

A. Determine the relationship between the sedimentary oxygen demand and flow velocities above the sediment bed. Use this information to develop criteria for the selection and placement of lake aerator capacity.

A.1. Narrative: Determination of the oxygen transfer rate across the water sediment interface is started with a boundary layer flow and mass transfer analysis and followed by laboratory experiments in which sediment is exposed to flow at different velocities. The information on oxygen uptake rates at different velocities is translated into recommendations for the placement of aeration devices away from the water/sediment interface.

A.2. Procedures: The boundary layer flow and mass transfer near a lake bed is analyzed taking into consideration intermittent flow as induced by internal wave motion. The oxygen uptake kinetics by bacterial and chemical processes are described similarly to models recently developed by Walker and Snodgrass (1986). Diffusion in and out of the sediments and through the water boundary layer above the sediments will be considered explicitly. Sediment motion (resuspension) is not a primary objective of this investigation since the velocities investigated are low. A theoretical relationship between sedimentary oxygen uptake rate and flow velocity is developed. This relationship is tested against experimental data which are collected in a laboratory flume. In the experiments oxygenated water is circulated at known low rates and velocities and DO profiles are measured. The reason for conducting the experiment in the laboratory and not in the field is to be able to measure the controlling parameters accurately, to control the flow conditions and to observe any changes near the bed visually.

Finally, the near-bottom velocities created by different typical aeration devices can be estimated depending on power input, design characteristics, distance from the lake bed, etc. Recommendations for the placement of such devices are developed to minimize sedimentary oxygen intake.

Field testing of the recommendations can occur as part of regular field applications and installations in the future. Concurrent field testing is not considered wise and not within the budget.

A.3. Budget:

a. Amount Budgeted: $63,000
b. Liquidation: $63,000
c. Balance: $ 0

A.4. Timeline for Products/Tasks

	July 91	Jan 92	June 92	Jan 93	June 93
Oxygen uptake analysis	————	————	——		
Preparation of experiment	————	——			
Preparation of instrumentation		————	——		
Experiments				———	
Data analysis				———	
Recommendation					———

A.5. Status:

The boundary layer flow and mass transfer near a lake bed have been analyzed theoretically for steady flow at velocities ranging from 0 to 0.25 m/s. Transfer of oxygen through the water boundary layer by forced convection and oxygen diffusion and uptake in the sediments were taken into consideration. An explicit

b. Institutional Affiliation:
St. Anthony Falls Hydraulic Laboratory, Department of Civil and Mineral Engineering, University of Minnesota.

c1. Summary of work accomplishments related to proposal.
Since 1975 principal investigator has conducted research and taught about flow, transport processes and water quality in lakes. Since 1986 research on bubble plume aeration and winter aeration of lakes have been conducted, and models and design procedures have been developed. During these studies the link between flow velocities and sedimentary oxygen demand has become apparent. Presentations of this previous work have been made at the 1st Minnesota Lake Management Conference (1989), the National NALMS Conference in 1988, the Minnesota Water Resources Conference in 1989, a Corps of Engineers Workshop in 1990.

c2. Principal publications related to the proposal.
"Lake Mixing Dynamics and Water Quality Models," H.G. Stefan, Journ. of the Minnesota Academy of Science, Vol. 55, No. 1, Oct. 1989.
"Oxygen Demand in Ice Covered Lakes as it Pertains to Winter Aeration," C. Ellis and H. Stefan, Water Resources Bulletin, AWRA, Dec. 1989.
"Lake Destratification by Bubble Plumes," by K. Zic and H.G. Stefan, Water Resources Research, 1990.
"Hydraulic Design of a Winter Lake Aeration System, C. Ellis and H.G. Stefan, Journ. of Env. Eng. ASCE, Vol. 115, No. 2, 1990.

2. Professors M. Semmens and J. Gulliver, the two program managers for objective B, are on the Civil Engineering faculty at the University of Minnesota, one specializing in physical and chemical processes for water and wastewater treatment, and the other specializing in contaminant transport. Each is widely published in their field. The program managers will be assisted by two graduate research assistants who will have a B.S. degree in science or engineering.

Program Manager: John S. Gulliver

a. Qualifications related to proposed work

B.S. 1974	University of California, Santa Barbara (Chemical Engineering)
M.S. 1977	University of Minnesota (Civil Engineering)
Ph.D. 1980	University of Minnesota (Civil Engineering)
1980–1981	Research Associate, University of Minnesota
1981–1987	Assistant Professor, University of Minnesota
1987–present	Associate Professor, University of Minnesota

b. St. Anthony Falls Hydraulic Laboratory, Department of Civil and Mineral Engineering, University of Minnesota.

c1. Summary of work accomplishments related to this proposal.
The principal investigator has been researching air–water oxygen transfer since 1977, including oxygen transfer in streams, oxygen transfer due to waves, and oxygen transfer at various hydraulic structures, such as spillways and overfall weirs. He has developed three measurements techniques for air–water transfer, and has undertaken numerous field and laboratory experiments. This research has been funded by the National Science Foundation, the U.S. Army Engineer Waterways Experiment Station, the U.S. Environmental Protection Agency (under the supervision of H. Stefan) and the LCMR.

The principal investigator was co–organizer of the Second International Symposium on Gas Transfer at Water Surfaces, in Minneapolis, MN in September 1990, and presented three papers at the symposium. Other presentations related to the topic have been at the National Conference on Hydraulic Engineering, the American Geophysical Union, the International Association for Hydraulic Research, Water Forum '86, and the American Water Resources Association.

c2. Principal publications related to this proposal.
Daniil, E.I. and J.S. Gulliver, "Temperature Dependence of the Liquid Film Coefficient for Gas Transfer," Journal of Environmental Engineering, ASCE, Vol. 114, No. 5, pp. 1224–1229, October 1988.

Gulliver, J.S. and M. Halvorsen, "Air–Water Gas Transfer in Open Channels," Water Resources Research, Vol. 25, No. 8, pp. 1783–1793, 1989.

Gulliver, J.S., J.R. Thene and A.J. Rindels, "Indexing Gas Transfer Measurements in Self–Aerated Flows," Journal of Environmental Engineering, Vol. 116, No. 3, pp. 503–523, 1990.

Gulliver, J.S. and H.G. Stefan, "Stream Productivity Analysis with DORM: 2. Parameter Estimation and Sensitivity," Water Research, Vol. 18, No. 12, pp. 1584–1595, 1984.

Rindels, A.J. and J.S. Gulliver, "Air–Water Oxygen Transfer at Spillways and Hydraulic Jumps, Proceedings, Water Forum '86, ASCE, Long Beach, California, August 1986.

Thene, J.R. and J.S. Gulliver, "Gas Transfer at Hydraulic Structures," National Conference on Hydraulic Engineering, ASCE, Colorado Springs, Colorado, 1988.

Gulliver, J.S. and M.J. Halverson, "Gas Transfer and Secondary Currents in Open Channels," Proceedings, Water Forum '86, ASCE, Long Beach, California, August 1986.

Program Manager: Michael J. Semmens, Ph.D., P.E.

a. Qualifications related to proposed work

1968	B.Sc., London University (Chemical Engineering)
1968-1969	Project Engineer, Hazen and Sawyer, Consulting Engineers, New York, NY
1970	M.S., Harvard University, Cambridge (Environmental Engineering)
1973	Ph.D., University College, London, England (Environmental Engineering)
1973-1977	Assistant Professor, University of Illinois
1977-1987	Associate Professor, University of Minnesota
1988-	Professor, University of Minnesota

b. Department of Civil and Mineral Engineering, University of Minnesota.

c1. Summary of work accomplishments related to this proposal.
The principal investigator has completed numerous studies that relate to the development of new technologies for the treatment of waters and wastewaters. In recent years he has focussed on the use of membranes for the removal of volatile organic contaminants from contaminated groundwaters. Since 1989 he has been studying the use of sealed end hollow fibers membranes for the transfer of oxygen to water, and has developed a model that describes the behavior of the gases inside sealed fibers. In 1989, a patent application was filed by Dr. Semmens on the design of a sealed-end fiber system that would allow for the escape of condensate from within the fiber. This important development overcame the problems that previous investigators had encountered and opened up a new opportunity for the development of a gas transfer that avoids bubble formation.

c2. Principal publications related to the proposal.

M.J. Semmens, R. Qin, and A. Zander, "Volatile Organics Separation from Water Using a Microporous Hollow Fiber Membrane," J. American Water Works Association, Vol. 81(4), pp. 162-167, 1989.

A. Zander and M.J. Semmens, "Membrane/Oil Stripping of VOC's from Water in a Hollow Fiber Contactor," J. Environ. Eng. Div. (ASCE), Vol. 115(4), pp. 768-784, 1989.

A. Zander, R. Narbaitz, and M.J. Semmens, "A Preliminary Pilot Scale Test of VOC Removal by Membrane Air Stripping," J. American Water Works Association, Vol. 81(11), pp. 76-81, 1989.

Semmens, M.J., D.M. Foster, and E.L. Cussler, "Ammonia Removal from Water Using Microporous Hollow Fibers," J. Membrane Science, 51 (1990), pp. 127-140.

Ahmed, T., and M.J. Semmens, "Use of sealed end fibers for Bubbleless Membrane Aeration: Experimental Studies," submitted J. Membrane Science, September 1990.

Ahmed, T., and M.J. Semmens, "The use of independently sealed microporous hollow fiber membranes for the oxygenation of water: Model development," submitted J. Membrane Science, September 1990.

VII. Reporting Requirements:

Semiannual status reports have been submitted January 1, 1992, July 1, 1992, and January 1, 1993. This is the final report. Technical details are contained in Project Reports No. 335, 344, and two under preparation from the St. Anthony Falls Hydraulic Laboratory.

1991 RESEARCH PROJECT ABSTRACT
FOR THE PERIOD ENDING JUNE 30, 1993
This project was supported by the Minnesota Future Resources Fund (MS 116.13)

TITLE:	Development and Application of Aeration Technologies
PROGRAM MANAGERS:	Heinz Stefan, John Gulliver, Michael Semmens
ORGANIZATION:	St. Anthony Falls Hydraulic Laboratory, Mississippi River at 3rd Avenue S.E., University of Minnesota, Minneapolis, Minnesota 55414 612-627-4010
LEGAL CITATION:	M.L. 91 Ch. 254 Sec. 14 Subd. 4(k)
APPROP. AMOUNT:	$148,000

STATEMENT OF OBJECTIVES
Two main objectives were pursued:
1) To determine the relationship between the sedimentary oxygen demand and water velocities above a lake sediment bed, and to use this information to develop recommendations for the placement of lake aerators and the selection of aerator capacity. Organic sediment is the main consumer of dissolved oxygen in winterkill lakes and in stratified lakes in summer.
2) To optimize the membrane aerator design. In hollow fiber membrane aeration, no bubbles are formed and 100% transfer efficiency is approached. Oxygen transfer correlations and an investigation of the impact of water quality upon performance are needed for scale up to field installations.
Both objectives were pursued by flow and mass transfer analysis and by laboratory experimentation.

RESULTS
1) The experiments and the analytical study have shown that sedimentary oxygen demand (SOD) increases in proportion to the velocity of the water moving over the sediments. Thus a tenfold increase in SOD occurs when the water velocity over the sediments increases, e.g. from 0.4 cm/s to 4 cm/s. Water velocities of this magnitude are generated naturally by wind. Water velocities near the sediment water interface are also created artificially by aeration devices. Required aeration capacity is usually estimated for quiescent water and hence underestimated when the aerators themselves cause a change in bottom lake water velocities. Laboratory measurements have given SOD rates between 0.2 and 6 $gm^{-2}d^{-1}$, depending on velocity from 0.1 to 10 cm/s. This is in agreement with the range of values determined for natural lakes either by oxygen budget calculations or field measurements.
2) The hollow fiber modules studied with LCMR funds are quite applicable as an in-stream aerator and a hypolimnetic aerator. The fibers are mounted in a cross-flow orientation to increase the transfer rate and utilize the naturally occurring flow. A parametric relationship has been developed based upon the results of laboratory experiments that relates to transfer rate coefficient to background velocity and the pressure in the fibers. This parametric relationship may now be used to predict the performance of an instream aerator or a hypolimnetic aerator in the field.

PROJECT RESULTS USE AND DISSEMINATION
The results from both objectives are summarized in project reports No. 344, 335, and two reports in preparation available free of charge upon request from the St. Anthony Falls Hydraulic Laboratory (612-627-4587). The results are also disseminated by conference presentation and publication in professional journals. Capacity estimation and installation of lake aeration equipment will become more reliable if the velocity effects identified and quantified in the study are included. The advantages to using microporous hollow fiber membranes for aeration are the control of the depth of aeration because there are no bubbles to rise, the minimal waste of the oxygen gas that is normally required, the control over the system that can be achieved by simply reducing the pressure inside the fibers, and the fact that a fiber module aeration system placed under the water would be relatively unobtrusive.

36 THE INFLUENCE OF WATER QUALITY ON BUBBLELESS MEMBRANE AERATION PERFORMANCE

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INTRODUCTION

The use of gas-permeable hollow-fiber membranes for water and wastewater aeration is a novel concept. In this process, pressurized, pure oxygen flows inside the fiber lumen, while water flows outside the membrane creating a high oxygen concentration gradient for the dissolution of oxygen across the interface without the formation of bubbles. Pressurized oxygen in the fiber produces a saturation concentration which is orders of magnitude higher than standard saturation conditions. Thus, the membrane aerator can oversaturate water with oxygen. High transfer rates are also aided by high surface areas. Small diameter fibers can provide large amounts of surface area per volume of water.[1] Various configurations of this process have been studied.[2-8]

In early field tests on membrane aeration, it was found that the oxygen transfer was better than that observed in clean water tests.[9] This effect may have been caused by the high organic content of the water in which the aerators were tested. Surfactants in small concentrations have been demonstrated to improve the performance of membrane aeration.[7] This paper explores the effect of organic surfactants on the oxygen transfer performance of a membrane aerator.

BACKGROUND

Membrane Types

Microporous membranes made from hydrophobic materials such as polypropylene (PP) and polyethylene (PE) are ideal for gas transfer into water. The pores in the membrane do not wet, but remain dry and gas-filled allowing for the rapid transport of oxygen through the membrane by gaseous diffusion. As a result, the membranes provide little resistance to gas transfer. Instead, the transfer is controlled by the liquid film resistance.

Unfortunately, porous membranes are limited to use at low gas pressures as bubbles form at high pressures. Electron scanned micrographs (ESMs) indicate that the porosity (interfacial area per fiber area) of the PP membrane is 30% to 40% while the PE membrane is approximately 3% to 5%. Elevated gas pressures lead to the formation and release of bubbles from the micropores. The pore dimensions determine the gas pressure required to form bubbles with larger pores bubbling at lower pressures. The PP membrane pore size distribution is wider than that of the PE membrane. The manufacturer of the PP (Hoechst Celanese, Charlotte NC) reports pore dimensions of approximately 0.05×0.15 microns; however, ESMs suggest pore diameters as large as 1 micron. ESMs of the PE fiber reveal a more uniform pore population with a diameter of about 0.2 microns.

A composite membrane (CM) provides a nonporous polyurethane layer (1 micron thick) between two porous polyethylene layers. Oxygen must dissolve into and diffuse through the nonporous layer which increases the effective resistance of the membrane. The cost of increased membrane resistance is offset by the ability to operate at higher gas pressures. ESMs reveal a CM porosity between that of PP and PE, and the pore diameters are relatively constant as in the PE membrane. Thus the CM has a high porosity and can be operated at high pressures.

47th Purdue Industrial Waste Conference Proceedings, 1992 Lewis Publishers, Inc., Chelsea, Michigan 48118. Printed in U.S.A.

Table I. Dimensionless Correlations

Reference	Correlation	Re Range
Yang and Cussler[14]	$Sh = 1.25\ (Rede/l)^{0.93}\ Sc^{0.33}$	5-3500
Ahmed[8]	$Sh = 0.0104\ Re^{0.806}\ Sc^{0.33}$	600-46000
This study	$Sh = 4.492\ Re^{0.324}\ Sc^{0.33}$	2000-14000

Module Configuration

Two types of membrane gas-transfer devices have been developed: flow-through and sealed-end. Flow-through devices, in which the oxygen flows in one end of the fiber and out the other end, have two major disadvantages in wastewater treatment. First, it is impossible to achieve 100% oxygen transfer efficiency because some oxygen is always vented, and second, volatile organic compounds (VOCs) present in the water can back-diffuse into the fiber lumen and be vented in the exhaust gas.[10-11]

Sealed-end devices eliminate these disadvantages. The sealed-end configuration does not allow gas to be vented and achieves transfer efficiencies approaching 100%. In addition, since no gases are vented, VOC stripping is eliminated. However, in the sealed-end device the back diffusion of nitrogen and water vapor change the oxygen partial pressure within the gas-filled fibers.[12] Water vapor will condense inside the fibers; in time, filling the fibers and stopping oxygen transfer. The back diffusion of gases has been modelled,[12] and the problem of condensed water collecting at the sealed end of the fiber has been overcome in a patented aerator marketed by Membran Corporation (Minneapolis, Minnesota).[13]

Theory

Transfer across an interface can be described by the following equation:

$$dC/dt = Ka(C^* - C) \qquad (1)$$

The reciprocal of the overall mass transfer coefficient reflects the resistance to mass transfer. 1/K, is equal to the sum of the reciprocals of the mass transfer coefficients for the liquid (K_L) and gas (K_G) boundary layers, and for the membrane (K_M).

$$1/K = 1/K_L + 1/K_G + 1/K_M \qquad (2)$$

For oxygen dissolution, $1/K_G$ is generally considered to be much less than $1/K_L$.[14] For a standard bubble aeration system, no membrane is used and K_M is not applicable; therefore, K is equal to K_L. This is also true for microporous membranes since $1/K_M$ is considered to be negligible. For composite membranes, the membrane resistance is more significant and K_M must be considered.

The specific surface area, *a*, is defined as the amount of interfacial area in a given volume of water. In standard aeration, this value depends on bubble size, gas flowrate, turbulence, etc., and it is difficult to quantify this term because of inaccuracies in measuring the number and diameter of the bubbles present in an aerated tank.[15]

Membrane aeration provides a fixed interfacial area. The membrane-water interface does not change with changes in water quality. This provides the opportunity to study the influence of water quality on the mass transfer coefficient directly.

Dimensionless Correlation

A dimensionless correlation has been developed to describe gas transfer across membranes by relating the Sherwood number to the Reynolds number and Schmidt number.[8,14] These correlations are presented in Table I.

Inspection of Table I reveals that the quotient, $Sh/Sc^{0.33}$, should be constant at a given Re, and its value should reflect the temperature corrected values of the mass transfer coefficient, K.

The dimensionless correlation for this study differed from previous correlations; however, differences in module configuration, flow regime, and the range of the Reynolds number prevent a direct comparison of these correlations. The flow-through module configuration of this study provided a constant oxygen partial pressure. Underestimation of the nitrogen concentration in previous sealed-end configurations could explain the lower performance observed by Ahmed (Figure 1). Also, the

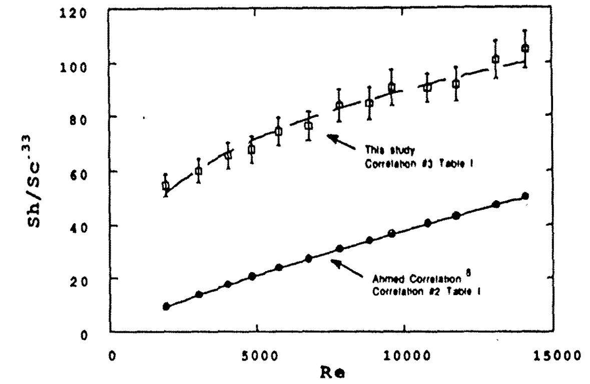

Figure 1. Clean water $Sh/Sc^{0.33}$ values using a polypropylene membrane aerator.

flow regime for this study was slightly different because both ends of the membrane aerator were fixed, as opposed to a fluidized sealed-end module studied by Ahmed. Water flow oriented perpendicular to the fibers (crossflow) has been shown to significantly increase the mass transfer rate.[14] Although the general water flow was parallel to the fibers in this study, there was some crossflow present before and after the fixed ends and the spacers which would tend to increase the mass transfer performance. Finally, the Reynolds number range of previous studies was four times larger than that of this study. These three reasons account for differences in the dimensionless correlations.

Pore Wetting

Pore wetting occurs when the surface tension of the gas-water interface in the pore is reduced such that the interface cannot be supported. This allows water to enter the pore. Larger pores will wet first. Once a pore wets, mass transfer through that pore is reduced significantly because the oxygen must diffuse through the pore by liquid diffusion rather than gaseous diffusion. The wetted pores effectively increase the membrane resistance, and this reduces the overall mass transfer coefficient. The oxygen transfer performance of a microporous membrane will decrease significantly once the pores begin to wet.

Surfactant Behavior

A surfactant is defined as any substance that, when dissolved in water in low concentrations, preferentially accumulates at interfaces, thereby reducing the surface or interfacial free energy. Surfactants have both a hydrophilic and a hydrophobic component. The hydrophilic moiety is ionic or highly polar, and depending on the type of functional group, the surfactant can be classified as anionic, cationic, or nonionic. The surfactants utilized in this study were anionic with a sulfate group functioning as the hydrophilic moiety. The hydrophobic moiety consist of a long carbon chain with nonpolar functional groups.

When a surfactant is added to water, the hydrophobic portions of the molecules tend to cause an increased degree of structure in the water. This increased water structuring increases the overall free energy of the solution. To minimize free energy, the surfactant migrates to the interface where orientation of the surfactant extends the hydrophobic group away from the water. As this process continues, two things happen: First, the hydrophilic groups stabilize the liquid boundary layer at the interface (liquid film stagnation). Second, the accumulation of surfactants at the interface results in a decrease of interfacial free energy, surface tension, and elasticity.[16]

The surface tension continues to decrease with the addition of surfactant until the critical micelle concentration (CMC) is reached. At this point surfactants from micelles which are clusters of surfactants with the hydrophobic tail oriented inward and the hydrophilic group on the outside. This "removes" the hydrophobic group from the water. A micelle will only form after the CMC has been achieved. The CMC varies with molecular weight and chemical structure of the surfactant.

Effects of Surfactants on $K_L a$

In standard aeration, as the surfactant concentration is increased, the decreased surface tension and elasticity of the interface leads to an increase in bubble break-up. This leads to a smaller bubble size and ultimately results in a higher a. However, the accumulation of surfactants at the interface tends to hinder transfer across the interface, and reduces the value of K_L. Surfactants increase a and decrease K_L at the same time.

Because of the limitations in measuring the interfacial area, the effect of water quality on K_L in standard aeration is difficult to assess. To eliminate the uncertainty in measuring interfacial area, a is combined with the mass transfer coefficient, and the product, $K_L a$, is characterized.

The Alpha Factor

Commonly, $K_L a$ is determined for an aerator under clean water conditions. The $K_L a$ determined under actual conditions is usually different, and its value is related to the clean water by an alpha factor.

$$\alpha = \frac{K_L a \text{ (process water)}}{K_L a \text{ (clean water)}}$$

The rate of oxygen transfer in process water is therefore given by:

$$dC/dt = \alpha K_L a\,(C^* - C) \qquad (3)$$

EXPERIMENTAL OBJECTIVES

The ability to measure K_L with a high degree of certainty is unique to membrane aeration. The primary objective of this study was to determine the effect of surfactants on membrane aeration, particularly K_L.

EXPERIMENTAL DESIGN

The experimental system utilized is shown in Figure 2. Water was drawn from the reservoir and pumped past the membrane module with a 1/15 hp, magnetic-drive pump (model AC-3C-MD, March Mfg.). The shell diameter of the membrane module measured 1/2 inch. The water flowed through the shell side of the module. A copper cooling coil was used to minimize variations in the water temperature, which was approximately 21° ± 1°. The effluent from the cooling coil returned to the water reservoir. The volume of the system was 4.7 liters, resulting in a reservoir residence time of 0.33 to 2.5 minutes depending on the water flowrate.

Flow-through membrane aerators utilized in this study were provided by Membran Corporation. The nitrogen content of the tap water was found to vary with water temperature, which led to uncertainty in the oxygen partial pressure inside the sealed-end fiber. This uncertainty was eliminated by sweeping the nitrogen out of the fiber with a flow-through device. A module typically consisted of 25 to 30 fibers with 58 cm of active transfer length. The outside diameters of the PP, PE, and CM fibers were 300, 412, and 270 microns respectively.

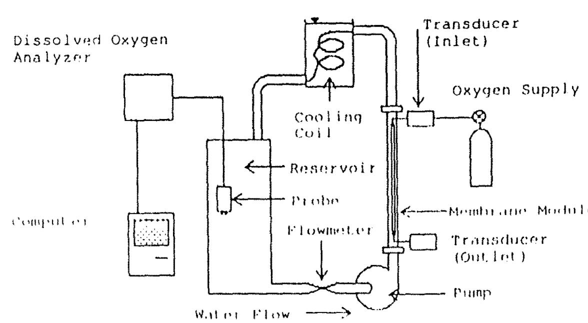

Figure 2. Experimental apparatus.

The dissolved oxygen in the reservoir was monitored with a dissolved oxygen analyzer (Royce model 9040). The analyzer was interfaced with a Macintosh SE which recorded dissolved oxygen and temperature measurements every 5 seconds. The oxygen gas pressure was measured with transducers in the influent and effluent gas lines connected to the membrane module.

The oxygen concentration in the water was increased from approximately 2 ppm to 8 ppm during each trial. The increase in dissolved oxygen was linear with time for the duration of the trial. The value of K_L was calculated with an average uncertainty of ± 8% using a first order-second moment uncertainty analysis technique.[17]

The mass transfer coefficient was determined by plotting $\ln(C^* - C_t/C^* - C_o)$ vs. time. The slope of this plot can be used to determine K.

$$K = \frac{v}{aL} \ln\left[1 - \frac{V}{Q}\,\text{slope}\right] \qquad (4)$$

Equation 4 can be derived from basic mass transfer principles and a mass balance on the reservoir.[12]

Five different surfactants were selected to provide a range in molecular weights, functional groups, and CMCs. These included four linear alkyl sulfates (LAS), (dodecyl, tetradecyl, heptadecyl, and octadecyl sulfate) and one alkyl benzene sulfonate (ABS), (dodecyl benzene sulfonate).

Tests were conducted at three Reynolds numbers: 1900, 5800, and 10800. Typical operational Reynolds numbers for full scale membrane aerators range from 2000 to 5000.

RESULTS

The clean water $Sh/Sc^{.33}$, representative of K_L, obtained from this study and based on the dimensionless correlation developed by Ahmed[8] are shown in Figure 1.

The clean water values obtained served as a control to evaluate the effect of the different surfactants. Figure 3 illustrates the effect of increasing surfactant concentration on $Sh/Sc^{.33}$ at three different Reynolds numbers using the PP membrane. A sharp decline in performance occured with only small doses of dodecyl sulfate. It is clear that at low surfactant concentrations, some resistance can be attributed to the liquid film because of the dependence on the Reynolds number. (Higher levels of turbulence decrease the liquid film thickness and increase performance.) However, at high concentrations of surfactants, the three curves converge and this suggests membrane transfer control.

Data similar to that presented in Figure 3 were collected using the four other surfactants with the PP membrane and are shown in Figure 4. An intermediate Reynolds number of 5800 was utilized. All surfactants caused a decrease in $Sh/Sc^{.33}$; however, a common trend based on SAA concentration was not apparent. Tetradecyl Sulfate and dodecyl benzene sulfonate are the notable exceptions. The tetradecyl had little effect on performance, while the dodecyl benzene decreased performance dramatically at very low concentrations.

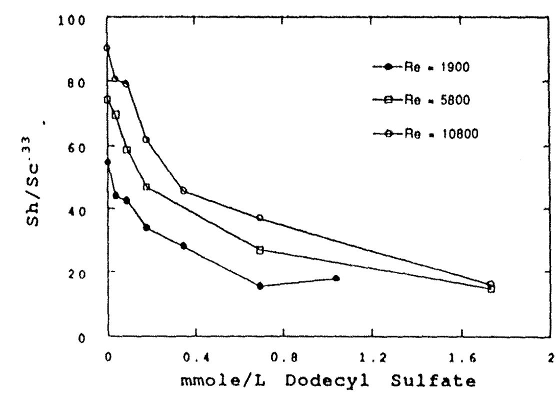

Figure 3. $Sh/Sc^{0.33}$ vs. concentration of dodecyl sulfate using a polypropylene membrane aerator.

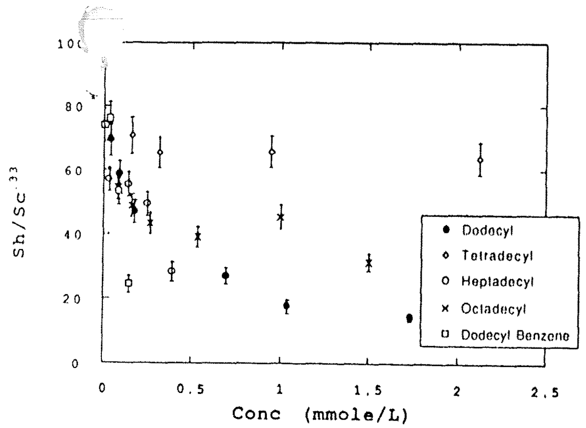

Figure 4. $Sh/Sc^{0.33}$ vs. concentration of five surfactants using a polypropylene membrane aerator.

The data shown in Figure 4 were analyzed further by measuring surface tension at the same surfactant concentrations utilized in the experimental studies. Surface tension was measured with a ring tensiometer (Cenco 70545, Fisher Scientific). The mass transfer data in Figure 4 were plotted versus surface tension and the results are presented in Figure 5. This graph illustrates a trend of decreasing $Sh/Sc^{.33}$ with decreasing surface tension. The impact on the mass transfer coefficient is pronounced when the surface tension falls below 50 dynes/cm. A possible explanation for this behavior is that the membrane is wetting at high surfactant concentrations.

The mechanism of pore wetting was supported by experiments using a methylene blue indicator. A porous hollow-fiber membrane was submerged in a container of tap water colored with methylene blue. The fiber was removed, and it maintained a white color. When surfactant was added to the solution in the same concentrations presented in Figure 4 and the experiment was repeated, the fiber retained a blue color which indicated that pores were wetting.

Figure 6 compares the performance of the PP, PE, and CM in the presence of dodecyl sulfate. All three membranes gave decreased performance as the surface tension decreased. Initially, the PP fibers exhibited the highest gas transfer performance and this may be attributed to its high porosity; however, the PP membrane was most strongly influenced by decreasing surface tension because of its larger pore size distribution. At surface tensions above 40 dynes/cm the PE and CM show a minimal decrease in performance because a small percentage of the pores are wetting. Below a surface tension of 40 dynes/cm, it appears that the majority of pores wet on all three types of membranes.

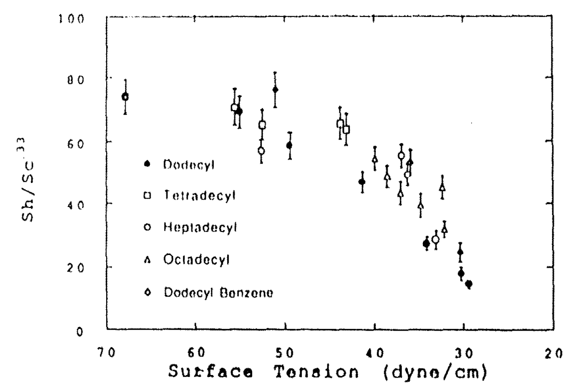

Figure 5. $Sh/Sc^{0.33}$ vs. surface tension for five surfactants using a polypropylene membrane aerator.

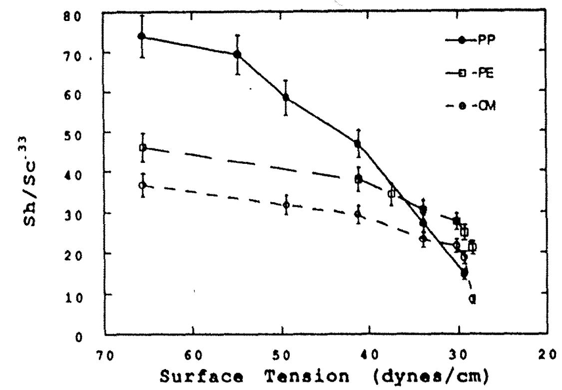

Figure 6. $Sh/Sc^{0.33}$ vs. surface tension for dodecyl sulfate using polypropylene, polyethylene, and composite membrane aerators.

FIELD RESULTS

Three sites have been tested to date: Lake Vadnais, a drinking water source for the city of St. Paul, MN; the Metro Wastewater Treatment Plant effluent stream in St. Paul; and an aquaculture facility near Morris, MN. All systems were tested with membranes in the sealed-end configuration.

The CM membrane has been tested at Lake Vadnais. Surface tension measurements on the lake water gave a value of 65.5 dynes/cm which is a little lower than that for clean laboratory water. The CM membrane has operated successfully for the last two months, and the performance is very close to that obtained in clean water.

PP and the CM membranes have been tested in the Metro secondary effluent stream which has a surface tension of 56.1 dynes/cm. The performance of the PP aerator fell to approximately 65% (α = 0.60 to 0.65) over a period of two months. The observed α for the CM aerator was approximately 0.6 after a month.

In the aquaculture test system the surface tension measured approximately 51 dynes/cm. The CM membrane was tested for 3 months. The performance dropped 15% to 20% (α = 0.8 to 0.85) during the first few weeks, and then performance stabilized.

DISCUSSION

Previous studies have indicated that the gas transfer performance of membranes has improved in waters with small amounts of surfactants present. Cote et al. studied gas transfer using nonporous silicone rubber membranes in the presence of commercial laundry soap (approximately 2×10^{-5} M expressed as dodecyl sulfate). They found that performance increased by 20% at Reynolds numbers comparable to the low Reynolds numbers in this study.[7] The Cote silicone rubber membrane was nonporous. Semmens et al. tested a nonporous siloxane-coated membrane and found a 40% increase in performance over clean-water studies during the first three weeks of operation.[9] The lake contained low concentrations of surfactant (Surface tension was approximately 65.5 dynes/cm).

In this study we found that surfactants decrease membrane aeration performance. However, two important differences between this study and previous studies exist: First, porous membranes were used in this study, in contrast to nonporous membranes used in previous studies. A nonporous membrane cannot wet; therefore, the pore wetting behavior witnessed in this study could not have occurred in the previous studies. Second, surfactant concentrations used in this study were significantly higher than the concentrations used in previous studies. High concentrations were deliberately utilized to identify the operational limitations of membrane aerators using porous membranes.

The field performance of the aerators may be compared to our experimental studies using Figure 6. The surface tension measurements for the wastewater treatment plant (WWTP), Lake Vadnais, and the aquaculture facility were 56, 65, and 51 dynes/cm respectively. The performance of the lake and aquaculture aerators were predicted by lab results.

At a surface tension of 51 dynes/cm, performance of the composite membrane drops by 15% according to Figure 6. This corresponds well to the alpha of 0.8 to 0.85 obtained in the aquaculture field study. Similarly, Figure 6 indicates that a surface tension of 65 dynes/cm would lead to no decrease in performance, and this was indeed the case at Lake Vadnais. However, the surface tension value of 56 dynes/cm, characteristic of the WWTP should have led to a 10% decrease for the CM membrane and 7% decrease for the PP membrane; when in fact, aerators which were operated at the WWTP experienced alphas in the range of 0.6 to 0.65.

Only one surface tension measurement was conducted at the Metro site, and the surface tension of the waste effluent could vary significantly on a day to day basis. We expect the membrane wetting will be determined by the minimum surface tension the membrane experiences. Since the pores cannot "unwet" if the surface tension rises it is possible that the surface tension fell below the measured value of 56 dynes/cm at some time during the field test. In addition, other factors such as biological fouling may have occured over portions of the membranes. Visible fouling did occur periodically; however, the membranes were scoured by maintaining a high flowrate (Re), and the degree of fouling was minimized.

Pore wetting was observed to be an "instantaneous" process in laboratory experiments. Decreases in field performance occured over a period of approximately one week or longer. The minimum surface tension may not occur immediately. It would take time to witness the lowest surface tension value. Biological fouling would also require time to develop. This provides an explanation for the observed alpha values for extended field studies which are lower than the predicted alpha values.

CONCLUSION

Effects of water quality on microporous membrane aerators have been evaluated. The ability of microporous membranes to effectively transfer oxygen is limited pore wetting, which becomes significant at surface tensions less than 40 dynes/cm.

The composite membrane offered the best performance for aeration. The pores of the outer microporous layer may wet; however, the nonporous layer allows high oxygen pressures to be maintained in the lumen of the fiber with minimal bubbling. The high oxygen pressure creates the driving force required for rapid oxygen transfer and this compensates for membrane resistance limitations.

Microporous membrane aeration performance does decrease with decreasing surface tension; however, the aerator will not fail until it is exposed to waters having an extremely low surface tension. At surface tensions above 50 dynes/cm, membrane aerators can still claim Standard aeration efficiencies of up to 8.0 lb of oxygen/hp/hr. Fifty dynes/cm is a low surface tension. In most applications the surface tension is greater than 50 dynes/cm as illustrated by the three field studies referenced in this paper. However, for waters with surface tensions below 50 dynes/cm, we recommend the use of a nonporous membrane aerator.

Notations

a = specific surface area (L^2/L^3)

C = water phase oxygen concentration (M/L^3)

C* = water phase oxygen concentration in equilibrium with the gas phase (M/L^3)

C_0, C_t = water phase oxygen concentration in the reservoir at time zero and time t respectively (M/L^3)

de = equivalent diameter of the system (L)

Diff = diffusivity of oxygen in water (L^2/t)

K = overall mass transfer coefficient (L/t)

K_L, K_G, K_M individual mass transfer coef. of gas, membrane and water respectively (L/t)

L = fiber length (L)

t = time

v = velocity of water (L/t)

V = volume of reservoir (L3)

Greek

ν = kinematic viscosity (L2/t)

Dimensionless Numbers

$$Re = \text{Reynolds Number} = \frac{v\,de}{\nu}$$

$$Sh = \text{Sherwood Number} = \frac{K_L\,de}{Diff}$$

$$Sc = \text{Schmidt Number} = \frac{\nu}{Diff}$$

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