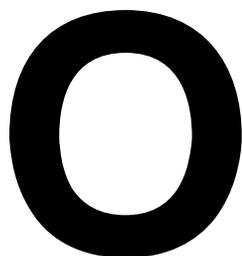


MEMBRANES

MEMBRANE CONTACTORS: AN INTRODUCTION TO THE TECHNOLOGY



Over the last 3 years, the designs of microporous membrane contactors for gas-transfer applications have rapidly developed. These newly designed contactors have moved the technology from small laboratory-scale devices, limited to 5 to 10 gallons per minute (gpm) capacity, to large-scale industrial devices designed for water treatment systems operating at 1,000 to more than 2,000 gpm. Since these devices are relatively new, the technology is often misunderstood. This article discusses the theory and principles of operation of membrane contactors in an effort to give users a better understanding of the technology.

Background

Membrane contactors are devices that allow a gaseous phase and a liquid phase to come into direct contact with each other, for the purpose of mass transfer between the phases, without dispersing one phase into the other. A typical use for these devices is the removal or dissolution of gases in water.

The concept of using membranes to bring two phases into contact with one another is not new. However, recent developments in the design of the contactors have greatly increased their efficiency and capacity. These developments have brought membrane contactors out of the laboratory and made them economical for medium- and large-scale industrial uses.

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For removal of dissolved gases from an aqueous stream, membrane contactors are operated with the aqueous fluid flow on one side of a hydrophobic membrane and a sweep gas and/or a vacuum applied to the other side of the membrane. Since the microporous membrane is hydrophobic, the membrane will not allow liquid water to pass through the pore into the gas side of the membrane. The membrane essentially acts as a support between the gas and liquid phases that allows them to interface at the pore. By adjusting the partial pressure of the gas in contact with the water, gases can be selectively removed or dissolved into the water.

Theory of Operation

Membrane contactors are typically fabricated with hydrophobic hollow-fiber microporous membranes. Since the membranes are hydrophobic and have small pores, water will not easily pass through the pore. The pressure required to force water to enter the pore can be calculated by the Young-Laplace equation modified for use with hydrophobic membranes (1, 2). This pressure is often called the breakthrough pressure (Equation 1).

$$P = -2\sigma\cos\theta/r \quad \text{Eq. 1}$$

where:

p = breakthrough pressure,

θ = contact angle,

σ = surface tension of the water, and

r = radius of pore in microporous membrane.

A hydrophobic polypropylene membrane with a pore size of 0.05 micron (μm) has a breakthrough pressure that exceeds 150 pounds per square inch gauge (psig). This high breakthrough pressure prevents water from passing through the membrane at pressures below 150 psig. At the pore, the gas phase will be in direct contact with the liquid phase. It is at this interface that gases can be removed or dissolved into the water, depending on the equilibrium condition established.

Principles of Operation

To explain the contactor's ability to remove dissolved gases from water, it is important to discuss the driving force for mass transfer. Henry's law states that the amount of gas that will dissolve into water at equilibrium is proportional to its partial pressure in the vapor-phase in contact with water (3) (Equation 2).

$$p = Hx \quad \text{Eq. 2}$$

where p = gas partial pressure,

TABLE A
Features and Benefits of the Membrane Contactors

Feature

Membrane contactors are not sensitive to flooding, channeling, or back-mixing.

Membrane contactors are modular.

Membrane contactors contain an order of magnitude greater surface area per unit volume as compared to conventional columns.

Membrane contactors can use a combination of vacuum and inert gas to create the driving force for mass transfer.

Benefit

Can be operated over a wide range of flowrates.

System footprint can be custom designed and modified.

Smaller overall system design.

Ability to achieve dissolved oxygen levels of 1.0 ppb

H = Henry's law coefficient, a function of water temperature, and
 x = concentration of dissolved solute at equilibrium.

Under one atmosphere and 25 °C, water will contain approximately 8.5 parts per million (ppm) of dissolved oxygen, 14.5 ppm of dissolved nitrogen, some trace amounts of carbon dioxide, and other trace amounts of gases found in the atmosphere. If the partial pressure of the gas in contact with the water is reduced, the amount of gas dissolved in the water will be reduced correspondingly. The partial pressure of the gas can be lowered in two ways. The total pressure of the gas phase can be lowered, or the concentration of the gases in the gas phase can be altered. To lower the total pressure of the gas, a vacuum can be applied to the gas side of the membrane. These same principles govern the operation of a vacuum tower (4). To alter the concentration of gases in contact with the water, a strip gas that contains little or none of the gas being removed from the water can be introduced into the gas side of the membrane. These same principles govern the operation of a forced-draft degasifier.

Pore Illustration

Since membrane contactors bring two phases in contact with one another for the purpose of transferring mass between the phases, their performance can be modeled using basic equations used for multistage columns. Their performance is typically measured by the ratio of the inlet-dissolved-gas concentration to the outlet-dissolved-gas concentration. Equation 3 (5) illustrates the ratio in its simplest form.

$$c_i/c_o = e^{-kaL/v_o} \quad \text{Eq. 3}$$

where c_i = outlet-dissolved-gas concentration,
 c_o = inlet-dissolved-gas concentration,
 k = mass-transfer coefficient,
 a = surface area,
 L = length, and
 v_o = velocity of the fluid.

The *mass-transfer coefficient* is a term that describes how quickly a mass can move through a medium. The resistance to transport can be described as the reciprocal of the mass-transfer coefficient. This concept is very similar to that of thermal conductivity and resistance in a heat exchanger. The overall mass-transfer coefficient is the sum of

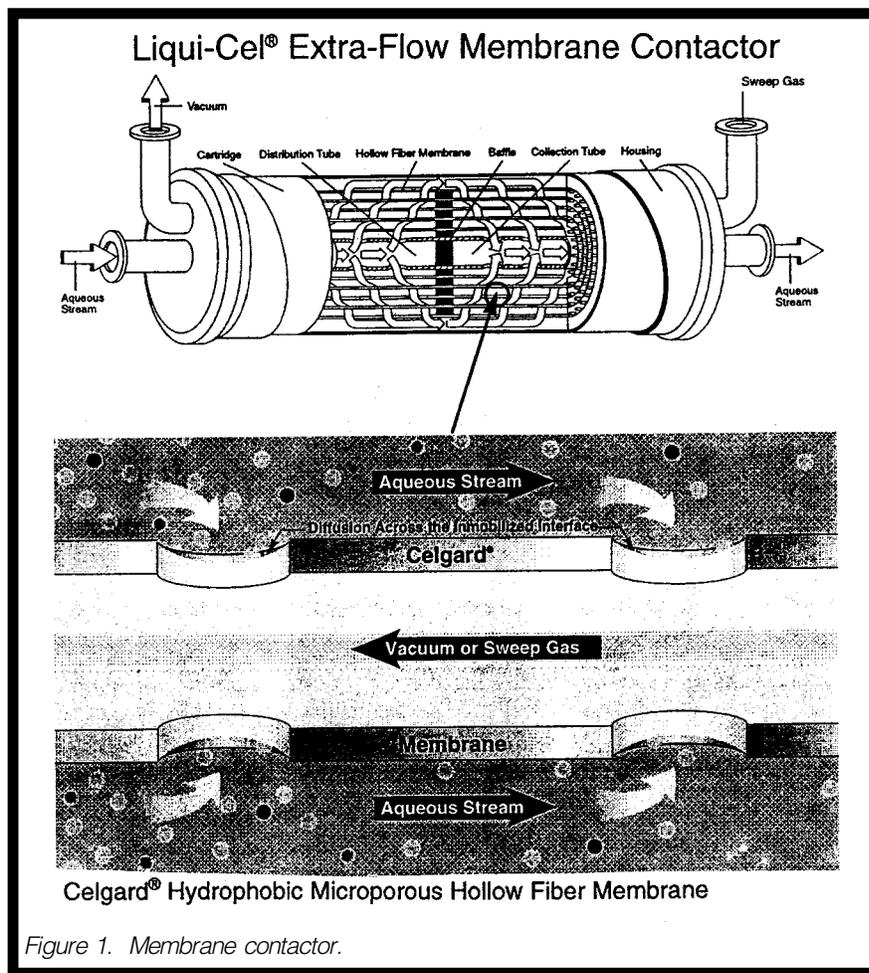


Figure 1. Membrane contactor.

the reciprocals of the individual mass-transfer coefficients. This can be written as shown in Equation 4 (5):

$$1/k_{ov} = 1/k_l + 1/k_m + 1/k_v \quad \text{Eq. 4}$$

where k_{ov} = the overall mass-transfer coefficient,
 k_l = the liquid-phase mass-transfer coefficient,
 k_m = the membrane mass-transfer coefficient, and
 k_v = the vapor-phase mass-transfer coefficient.

As a gas molecule diffuses through the water, it must travel around water molecules. As it reaches the pore, it must diffuse through the gas molecules inside the pore and into the other side of the membrane.

Yang and Cussler (6) have published a paper titled "Designing Hollow-Fiber Contactors" that experimentally verifies that the dominant resistance to mass transfer for oxygen is in the water phase. The gas phase and membrane resistances were found to be so much smaller as to be negligible. The correlation for the mass-transfer coefficient for flow in-

side a hollow fiber and outside a hollow fiber are listed below. Since the water phase is the dominant resistance, it is understandable that the mass-transfer coefficient can be correlated to the velocity of the water in contact with the membrane. These correlations have been published by Reed, Semmens, and Cussler (5) in *Membrane Separations Technology, Principles and Applications* (Equations 5 and 6).

Water flowing inside the hollow fiber:

$$kd/D = 1.62(d^2v/LD)^{1/3} \quad \text{Eq. 5}$$

Water flowing outside and perpendicular to the hollow fibers:

$$kd/D = 1.4(dv_o/D)^{1/3} \quad \text{Eq. 6}$$

where k = mass-transfer coefficient,
 d = fiber diameter (inside for Equation 5 and outside for Equation 6),
 D = diffusion coefficient of oxygen in water,
 v = actual water velocity,
 L = length of the contactor, and
 v_o = superficial water velocity.

Performance Data

As can be seen from Equations 5 and 6,

the performance of the contactor can be correlated to the velocity through the contactor, the area of the contactor, the diameter of the fiber, and the diffusivity of the gas in the liquid. For a given contactor design, the performance can be described as a function of the water flowrate. A graph showing the removal performance of a contactor over a range of flowrates is provided in Figure 2.

The efficiency with which a contactor can remove dissolved oxygen from water is typically used to describe the contactor's performance. Oxygen is used because it can be accurately measured and it is the gas most commonly removed from water. The percentage of oxygen removal is defined through Equation 7.

$$[(C_i - C_o)/C_i] * 100 \quad \text{Eq. 7}$$

where C_i = inlet concentration and C_o = outlet concentration.

The performance of the device is typically referred to in terms of % oxygen removal. The outlet concentration can be quickly calculated from the inlet concentration and the % removal value.

When data are presented as the outlet dissolved-oxygen concentration, it is important to know the inlet concentration of the oxygen. For example, water at 25 °C will contain approximately 8.5 ppm of dissolved oxygen, and at 20 °C it will contain approximately 9.1 ppm of dissolved oxygen. Without knowing the inlet concentration, the % removal of the device is not known.

Contactor Evolution

Early contactors were made of microporous hollow-fiber bundles in a shell-and-tube configuration. The liquid phase was introduced into the inside of the hollow fiber (lumen-side), and the gas phase was introduced on the outside (shell-side). The gas phase flowed parallel to the water phase. This design suffered a major drawback: the hydraulic resistance to flow through the inside of the hollow fiber. This resistance created an unacceptably high pressure drop. The maximum flowrate commercially available for these devices was typically around 5 gpm. To accommodate a higher flowrate with lower pressure drop, contactors were placed in parallel to increase capacity.

Initial attempts to increase the individual capacity of the contactors were unsuccessful. The capacity could be increased by increasing the contact area

or by reducing the waterside pressure drop. The contact area could be increased by increasing the bundle diameter or the length of the contactor. Fabricating a contactor with a large-diameter fiber bundle proved to be difficult. The depth of the bundle prevented the potting material from completely filling the voids between the fibers. This made a fragile bundle that did not hold up well over time. Attempts to reduce the waterside pressure drop included increasing the fiber diameter and flowing water on the outside of the fibers. Increasing the fiber diameter adversely affected the amount of contact area that could be packed into the device. Contactors designed with water flow on the outside of the bundles showed poor performance caused by severe flow channeling.

A baffled device that overcame these hurdles was patented¹ (7) in 1993. In this design, the hollow fibers are woven into a fabric array. The fabric is wound around a central distribution tube. During the winding process, a baffle is placed at the center of the bundle. This patented design allows water to flow radially across the fiber bundle and be evenly distributed throughout the bundle (Figure 1).

This design reduced the waterside pressure drop through the contactor and allowed additional membrane area to be incorporated into a single device. Figure 3 shows the pressure drop of the contactor as a function of flowrate. As can be seen from the attached graph, the pressure drop of the contactor with flow inside the hollow fiber is greater than that with flow on the outside of the hollow fiber.

The importance of this reduction in pressure drop is not intuitively obvious. When the pressure drop is reduced, two and three contactors can be placed in series. Placing the contactors in series greatly improves the overall removal efficiency of a contactor train by increasing the fluid velocity. Figure 4 shows the performance of one and two contactors in series as a function of flowrate. The slope of the curve representing the performance of one contactor has a steeper negative slope than does that of the two contactors in series. This can be explained by reviewing the mathematical equations.

As described in Equation 7, the percentage of removal is defined as the inlet concentration-outlet concentration/inlet concentration for one contactor in series. The second contactor in a series

TABLE B
Common Terms Used with
Membrane Contactors

Excess sweep: The gas flowrate required to maximize the performance of the contactor.

Lumen-side: Inside the hollow fiber.

Partial pressure: The pressure exerted by a single component of a gas mixture.

Shell side: Outside the hollow fiber.

Shell: The housing containing the membrane contactor.

Solute: Species transferred between phases.

will theoretically have the same removal efficiency. For example, at 100 gpm, the first contactor in series removes approximately 95% of the dissolved oxygen. The second contactor in series will remove 95% of the remaining dissolved oxygen, or 99.75%. As can be seen from the graph, the flowrate through two contactors in series can be increased to more than 200 gpm while achieving the same removal efficiency.

A graph plotting the mass-transfer coefficient as a function of flow per unit area is shown in Figure 5. The actual value for the mass-transfer coefficient is obtained by measuring the performance of the contactor and solving for the mass-transfer coefficient, k . It is interesting to note that the mass-transfer coefficient for a given fiber is higher when the liquid phase is outside the fiber. The enhanced mass transfer is attributed to the additional turbulence associated with flow across the membrane.

Comparison to Conventional Membrane Filtration

The use of membranes in membrane contactors is very different from how membranes are used for liquid filtration. Filtration devices, used to remove particles and dissolved solids from water, allow the water to pass through the membrane; and they exclude particles or dissolved solids from passing through the membrane based on the sizes of those particles or solids. Water pressure is used as the driving force to move the water through the membrane, and the pore excludes particles from pass-

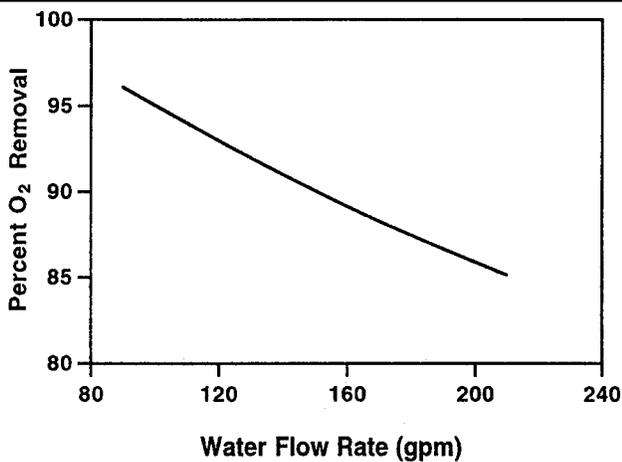


Figure 2. Flowrate versus removal performance of a contactor operated with a nitrogen sweep gas (water temperature 20°C).

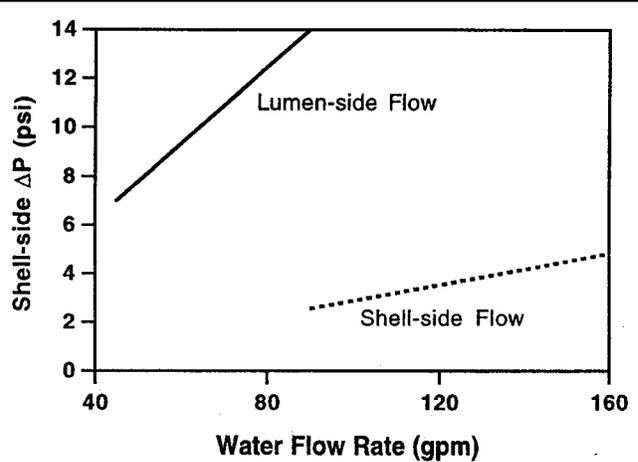


Figure 3. Flowrate versus pressure drop for flow inside and outside of the fiber.

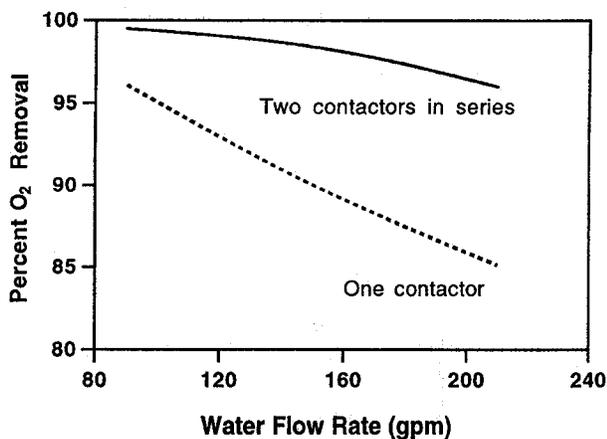


Figure 4. Flowrate versus removal performance of a contactor for one and two in series operated with nitrogen sweep gas.

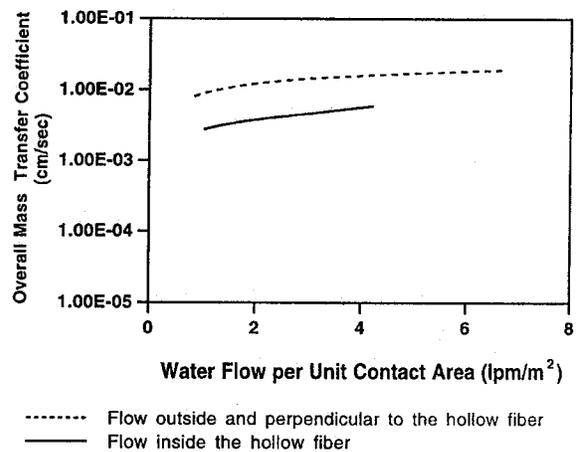


Figure 5. Flow per unit area versus mass-transfer coefficient for flow outside and perpendicular to fiber, and flow inside fiber.

ing through the membrane. Reverse osmosis, ultrafiltration, and microfiltration membranes are not capable of removing dissolved gases.

Membranes used for phase-contact purposes have no convective flow across the membrane. A partial pressure gradient is used to facilitate the transfer of mass via diffusion from one phase to another. Lowering of the partial pressure of the gas in contact with the water allows dissolved gases to be removed or dissolved. Liquid water does not pass through the hydrophobic membrane; the membrane is used merely to support the two phases and to allow them to contact one another.

Filtration membranes are typically qualified by the percentage of a particular size of particle or solute that the membrane is capable of removing. Since membrane contactors are essentially devices that bring two phases in contact with one another for the purpose of mass

transfer, their performance is typically measured by the ratio of the inlet-dissolved-gas concentration to the outlet-dissolved-gas concentration.

The most closely related membrane technologies to the membrane contactors are pervaporation and gas separation. Both of these technologies use nonporous membranes that selectively allow only certain species of gases to permeate through the membrane. In contrast, membrane contactors contain microporous membranes. Membrane contactors are nonselective and will allow all gases to pass through them.

Comparison to Existing Technology

Vacuum towers work under the same principles as membrane contactors. They are typically tall columns filled with packing or trays and are used to bring a liquid phase in contact with a gas phase for the purpose of removing dissolved gases from the liquid. The liquid runs

from the top of the column down around the packing. The packing creates a large surface area for the gas phase to contact the liquid phase. Membrane contactors perform the same task; however, they bring the two phases into contact at the pore without needing to disperse one phase into the other. Table A lists some benefits of membrane contactors.

Conclusion

These recent developments have enabled the membrane contactor technology to progress from the laboratory into large-scale production facilities. The most difficult obstacle to overcome was the reluctance of designers to accept new technology, even though traditional mass-transfer concepts are employed. These devices have become widely accepted in many markets, including the semiconductor, power, and pharmaceutical markets. Other markets are

expected to emerge as engineers become more familiar with the technology. Table B gives a glossary of some common terms associated with membrane contactors. ■

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Endnote

¹Patented by Hoechst Celanese Corp. in 1993.

Author Fred Wiesler is a senior technical service engineer with Hoechst Celanese Separations Products Division in Charlotte, N.C. He has more than eight years of membrane-related experience, four of which have been spent working with membrane contactors.

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