

DEAERATION

DEGASIFICATION OF WATER USING NOVEL MEMBRANE TECHNOLOGY

Dissolved oxygen, nitrogen, and carbon dioxide are naturally present in water. Dissolved gases should be carefully monitored and controlled, as they can affect the products and processes in which the water is used. For example, dissolved oxygen can react with metals, forming an oxide layer on the surface of finished products or piping material. Also, as the water temperature is increased, dissolved gases can form bubbles that may lead to incomplete wetting of surfaces. The removal of dissolved gases is an important processing step and is routinely accomplished with a vacuum degasification column or with chemicals. Removal of specific gases, such as oxygen, can also be accomplished by stripping the gases from the water using a vacuum and/or an inert gas such as nitrogen.

Membranes have been used to degasify water for more than 20 years in laboratory environments. One major drawback of the membranes has been their inability to handle industrial-size flowrates efficiently. Because of this low capacity, membranes have been viewed as small-scale devices. Over the last several years, new designs have recently been developed to overcome the capacity limitations. Degasification membrane modules, also called *membrane contactors*, and designed to handle industrial-size flowrates, are now commercially available. This paper dis-

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cusses the theory behind membrane degasification and its evolution over the last few years.

Background

In order to best explain the operation of membrane-based degasification systems, it is important to review the laws governing ideal gases. These relationships govern the operation of the membrane contactors as well as that of conventional degasification columns.

Dalton's law states that the total pressure of a gas mixture is equal to the sum of the partial pressures of the individual gases in the gas mixture (Equation 1):

$$P_{\text{total}} = P_1 + P_2 + P_3 + \dots \quad \text{Eq. 1}$$

The partial pressure component of each gas can be rewritten as in Equation 2:

$$P_{\text{total}} = P_{\text{total}}y_1 + P_{\text{total}}y_2 + P_{\text{total}}y_3 + \dots \quad \text{Eq. 2}$$

where y_n = the mole fraction of the component.

These relationships tell us that the pressure that a gas will exert in a fixed volume is dependent on the total pressure of the gas mixture and on the individual concentration of the gas in the mixture (1). This is an important relationship that is used to create the driving force to remove or dissolve gases into water.

Henry's law states that the solubility of a gas in water is directly proportional to the partial pressure of that gas. This relationship is generally valid at low dissolved-gas concentrations (2).

$$P_1 = H^x \quad \text{Eq. 3}$$

where P_1 = partial pressure of the gas; H = the Henry coefficient for that gas (this value can be found in engineering tables); and x = concentration of dissolved gas.

This law tells us that the amount of gas that will dissolve in water is proportional to its partial pressure. We know from

Dalton's law that the partial pressure of a gas is directly proportional to its concentration in the gas phase. From these two relationships we can determine a particular gas equilibrium concentration in the aqueous gas phase if we know the total gas pressure and the concentration of that component in the gas phase.

Mass Transfer

In order to transfer a dissolved gas from an aqueous phase into the gaseous phase, there must be a driving force. The driving force utilized with a membrane contactor is a concentration (or partial pressure) difference. From Henry's law, we note that if we reduce the partial pressure of a gas we can reduce the amount of that gas that will remain dissolved in water. So, if we reduce the partial pressure of the gas, some quantity of dissolved gas will come out of solution until the system reaches equilibrium. From Equation 3, we can see that the partial pressure of a gas is equal to the product of the total gas-phase pressure and the concentration of the gas in the gas phase. The partial pressure of the gas can be reduced by lowering the total pressure of the gas phase and/or by lowering the concentration of the individual gas in the gas phase. These same principles govern the operation of a conventional degasification column.

For example, water that has been in contact with air and has been allowed to reach equilibrium contains a certain quantity of dissolved nitrogen and dissolved oxygen gas. The amount of each gas that dissolves into the water is proportional to the partial pressure of the gas in air. If this water is exposed to a nitrogen environment, such as a nitrogen blanket, dissolved oxygen will be removed and nitrogen will be dissolved into the water. The oxygen tends to leave the aqueous phase because of the change in concentration and corresponding partial pressure of the oxygen in the gaseous phase. The nitrogen tends to dissolve into the water because of an increase in concentration and partial pressure in the gaseous phase. Similarly, if the water is exposed to a vacuum,

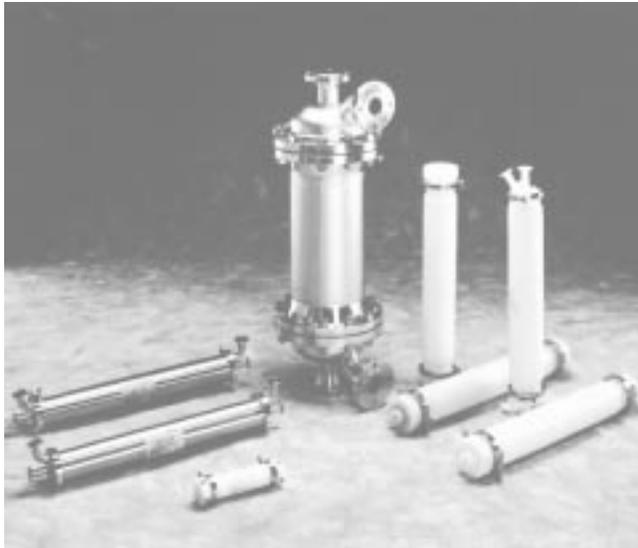


Figure 1. Oxygen removal devices.

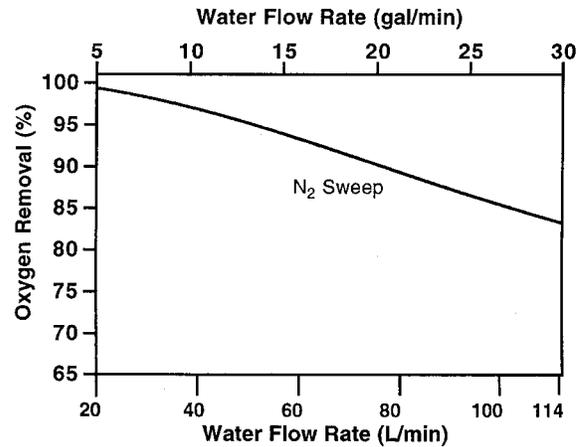


Figure 2. Oxygen removal performance of a 4-inch-diameter membrane contactor (19 m² area).

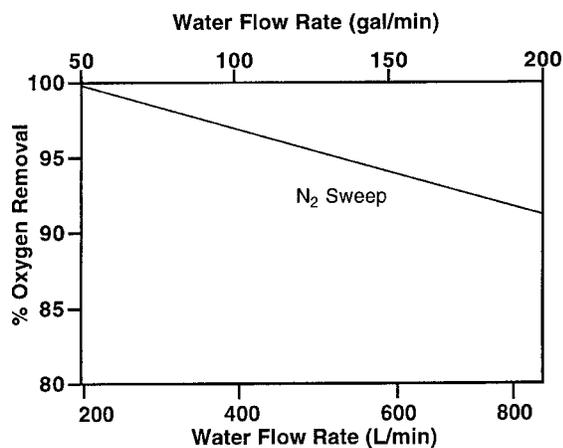


Figure 3. Oxygen removal performance of a 10-inch-diameter membrane contactor (135 m² area).

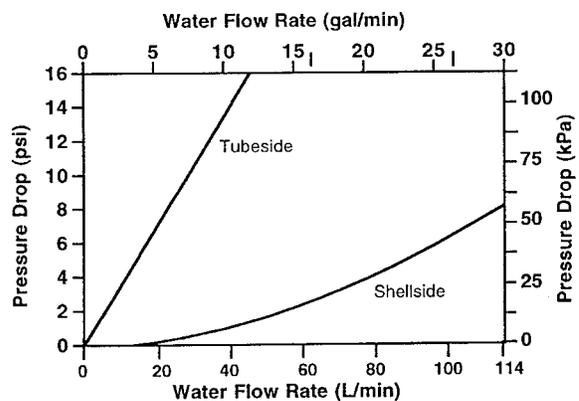


Figure 4. Pressure drop through a 4-inch-diameter membrane contactor.

the total gas-phase pressure and corresponding partial pressure of the gases will be reduced and both gases will be removed from the water.

Membrane Contactor Theory

Membrane contactors are typically shell-and-tube devices containing microporous hydrophobic hollow fibers. Since water will not pass through the pores, the membrane surface acts as an inert support that allows water to come into direct contact with a gas phase without dispersion. The partial pressure of a gas can be adjusted to control the amount of that gas that will dissolve into water.

Since a membrane contactor contains many small-diameter fibers, the interface between the gas and liquid phase becomes very high. In fact, the contact area per unit volume ratio is typically an order of magnitude greater than that for a conventional packed column. This concept can greatly reduce the size of a degasification system.

The rate at which the gas will leave the water and enter the gas phase is limited by three resistances:

1. The resistance that the molecules of dissolved gas will encounter when traveling through the water;
2. The resistance that the molecules of

dissolved gas will encounter when they travel through the membrane; and

3. The resistance that the molecules of dissolved gas will encounter when they travel through the gas away from the membrane.

For typical inert gases such as nitrogen and oxygen, the liquid-side membrane resistance will be the dominant resistance, and the other resistances can be assumed to be negligible (3).

Evolution

The first-generation membrane

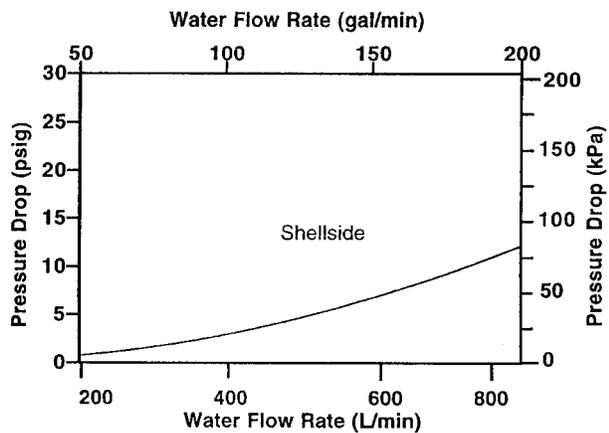


Figure 5. Pressure drop through a 10-inch-diameter membrane contactor.

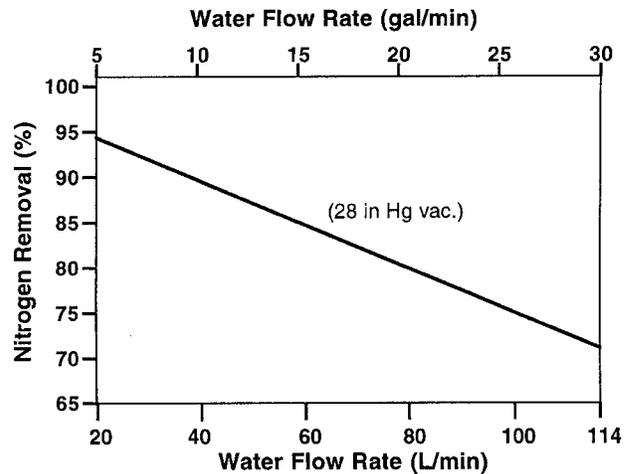


Figure 6. Removal efficiency of nitrogen under vacuum conditions.

contactors were simply bundles of hydrophobic fibers placed into a shell. Water was pumped through the inside of the hollow fiber and gases were passed across the outside. The flowrate through the device was limited by the pressure drop associated with the liquid flow through the hollow fibers, and mass transfer was inhibited by the laminar flow limitations of the liquid flow (4). The devices were limited to low flowrates, and systems were oversized to make up for the low mass-transfer rates.

Over the last several years, a novel membrane contactor design was developed that has dramatically increased the flow capacity of these devices up to 200 gallons per minute (gpm). This patented new design incorporates a hollow-fiber fabric array that is wound around a central distribution tube with a central resin baffle. This patented design allows for turbulent flow on the outside of the hollow fiber (5). The fiber is arranged in a uniform open packing that allows for a greater flow capacity and utilization of all of the membrane area. Water flows radially across the membrane, which induces local turbulence that increases the mass transfer in the water phase, the dominant mass-transfer resistance in a membrane contactor. Photographs of these devices are shown in Figure 1.

A typical membrane contactor contains thousands of microporous polypropylene hollow fibers woven into a fabric array. By adjusting the concentration of the gases on the inside of the fiber, the concentration of dissolved gases in the aqueous phase, outside of the fiber, can be controlled.

Oxygen Removal Performance

Figures 2 and 3 show the oxygen removal performance as a function of water flowrate of two commercially available membrane contactors. Figure 2 shows the flow versus percentage of oxygen removal of a 4-inch-diameter membrane contactor. Figure 3 shows the same curve for a 10-inch-diameter contactor. Both graphs were generated using a nitrogen sweep inside the hollow fiber.

As can be seen from these two graphs, the 4-inch contactor can remove approximately 90% of the dissolved oxygen at 20 gpm, and the 10-inch will have approximately the same removal efficiency at 200 gpm. The high capacity of the 10-inch-

diameter contactor has allowed the membrane contactors to be utilized in systems with larger flowrates. This high-capacity contactor has provided system design engineers an option to replace conventional degasification technologies for low flowrates as well as for flowrates exceeding 1,000 gpm.

Figures 4 and 5 show the pressure drop of the same two membrane contactors as a function of flowrate. Figure 4 shows two curves, one describing the pressure drop associated with flow inside the hollow fiber (tube side), and the other describing the pressure drop associated with flow on the outside (shell side) of the hollow fibers. As can be seen from the graph, the pressure drop of the contactor with flow inside the hollow fibers is much greater than the pressure drop of the same contactor with flow outside the fibers. This can be attributed to the larger and more open flow area available in the shell-side design.

As can be seen from the pressure-drop curves (Figures 4 and 5), the maximum capacity of the 4-inch-diameter contactor is about 30 gpm (114 liters per minute [L/min]), and the 10-inch-diameter contactor has a maximum capacity of 200 gpm (760 L/min). The pressure drop for each of these devices at their maximum capacity is less than 10 pounds per square inch gauge (psig). This low pressure drop allows these devices to be placed in series. The ability to place these contactors in series allows the overall efficiency to be increased. For example, if three 10-inch contactors are placed in series in a 150-gpm stream, the first contactor will remove approximately 95% of the dissolved oxygen, the second will remove 95% of the remaining dissolved oxygen, and the third will remove an additional 95% of the remaining dissolved oxygen. This allows the contactors to remove 99.99% of the dissolved oxygen from the 150-gpm water stream with less than a 15-psig pressure drop.

Carbon Dioxide Removal Performance

The membrane contactors can be used to remove a variety of gases from water. When removing a reactive gas such as carbon dioxide, it is important to examine reaction kinetics and its effect on mass-transfer rates. The membrane can remove only dissolved species that exert a partial pressure and are volatile. Therefore, only the free carbon dioxide can be removed, not the carbonate or bicarbonate forms. The membrane

cannot remove the ionic species. The amount of carbon dioxide that will be removed is typically reported as a percentage of the dissolved-gas component.

Nitrogen Removal Performance

Nitrogen exists as a dissolved gas and does not dissociate in water. Under ambient conditions under 1 atmosphere of air, water will contain approximately 14 parts per million (ppm) of dissolved nitrogen and 8.5 ppm of dissolved oxygen. Test results indicate that oxygen and nitrogen are removed at approximately the same rate. This can be attributed to the similarity in sizes and weights of the oxygen and nitrogen molecules. Since they are similar in size and weight, the liquid-phase resistances are similar. Figure 6 shows the removal efficiency of nitrogen under vacuum conditions.

System Design

Over the last few years, membrane contactors have become viable alternatives for dissolved-gas removal from water. The membrane design has been improved to overcome hydrodynamic pressure-drop resistances, allowing individual contactors to handle an excess of 200 gpm. Because of the contactors' low pressure drop, they can be placed in series to increase their oxygen removal efficiency.

The membrane contactor allows for some unique design considerations. Because of their nondispersed immobilized gas liquid interface, membranes can be operated over a wide range of flowrates without affecting the effective contact area for mass transfer. The interface is unaffected even when the contactor is exposed to sudden changes

in flow. Because of the uniform membrane packing structure of the device, the sweep gas consumption or vacuum pump size can be minimized. The modular design allows for systems to be built with a low profile, and can be tailored for each application.

Conclusions

Membrane contactors utilize the same basic gas laws that govern the operation of conventional degasification columns. The membrane contactors simply bring the gas and liquid phase into contact with one another at a hydrophobic pore rather than by dispersing the liquid phase into the gaseous phase.

Membrane contactors have been available for laboratory-scale applications for many years. The recent capacity and performance evolution has brought them out of the laboratory and into the full-scale manufacturing facilities. Some of these facilities use membranes to process over 1,000 gpm of deoxygenated water.

The technology is still new to many design engineers and endusers. Over the last several years, these high-capacity membrane devices have proven their integrity and have rapidly grown market acceptance. Their use in water systems is made attractive by many unique characteristics:

1. The modular design, like that of filtration, reverse osmosis, and ion exchange, allows the entire water system to be designed with flexibility.
2. The nondispersive design eliminates system upsets that occur during start-up and changes in flowrate.
3. The membrane device and housing make it possible to design an eco-

nomical "closed" system for gas removal. ■

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