carbon dioxide and dissolved oxygen removal from makeup water by gas transfer membranes

Authors: S.H. Macklin, Northeast Utilities, W.E. Haas, SUEZ and W.S. Miller, SUEZ

summary

New membrane processes for water treatment are continually being sought after for their simple and continuous operation. A new approach for removing dissolved gases from make-up supplies utilizes hydrophobic hollow fiber membranes. These membranes have many characteristics that enhance or replace other degassing methods. This paper reports carbon dioxide and dissolved oxygen removal efficiencies for a 100 gpm gas transfer membrane unit installed in a nuclear power plant’s make-up system.

introduction

Several dissolved gases concern the water treatment industry. The most common are oxygen, carbon dioxide and hydrogen sulfide. These gases exist naturally in many water supplies. Removing, adding or controlling the dissolved concentration of these gases depend on the water treatment user’s pure water requirements. For instance, controlling carbon dioxide concentration is important for the beverage industry. Municipalities remove hydrogen sulfide gas, improving drinking water taste. And, utilities remove oxygen from boiler feed makeup to prevent corrosion. Removing these gases prior to, or during ion exchange demineralization, can have a significant impact on operating performance and efficiency. The conventional water treatment arsenal available for dissolved gas removal includes:

- Aeration (open and forced draft).
- Cold water vacuum deaeration.
- Hot water steam injection/stripping deaeration.
- Oxidation/reduction reaction chemicals.
- Ion exchange processes.

Removing dissolved gases from water with Gas Transfer Membranes (GTM*) is a proven, low flow rate laboratory technology. Recent advances in GTM design now make them feasible for high flow rate industrial systems. Using these systems alone or in conjunction with other membrane processes offer new or improved options for water treatment.

This paper briefly describes the theory behind GTM units and how they complement reverse osmosis (RO) and catalytic oxygen removal technology. We also present carbon dioxide (CO₂) and oxygen (O₂) removal test data from a makeup water treatment system at a nuclear utility.

GTM principles

The GTM tested utilizes hollow fiber hydrophobic polypropylene membranes. This membrane is gas permeable and water impermeable. The hollow fiber configuration, with the gas phase inside the fiber, offers high surface area for maximum contact time. The patented Liqui-Cel (registered trademark of Celgard, LLC) design tested includes an internal baffle to promote turbulent flow in and around the hollow fibers.

Each thread-like fiber has a 300 micron outer diameter with 0.05 micron gas permeable pores.

As characteristic with membrane processes, three streams are identifiable:

- Feed stream.
- Process effluent.
- Concentrate waste stream.
As illustrated in Figure 1, the tube interior operates under vacuum, nitrogen sweep gas or both in combination. Dalton’s Law of Partial Pressure and Henry’s law of Gas Solubility define the mechanisms that drive dissolved gas removal by GTM. In short, reducing the gas concentration over the water allows the dissolved gases to expand into the hydrophobic hollow fiber and be swept away. Reducing the CO\textsubscript{2} and O\textsubscript{2} gas concentration is accomplished by applying a vacuum, using inert nitrogen sweep gas or combining both.

**Figure 1: Liqui-Cel GTM unit**

**test site**

Northeast Utilities Millstone Nuclear Power Station is located in Waterford, CT. The station consists of three independent units. Unit 1 is a General Electric 650 MW boiling water reactor (BWR) design, commissioned in 1970. Unit 2 and 3 are pressurized water reactors (PWR). Unit 2 is a Combustion Engineering 850 MW design commissioned in 1975. Unit 3 is a Westinghouse 1150 MW design, commissioned in 1986.

The plant’s makeup water is deoxygenated and demineralized by a service contract company. Unit 1 and 2 share the same makeup water treatment system and operate independently from Unit 3’s makeup system. We selected Unit 3’s makeup system for the test site based on its design and Northeast Utilities’ long history for supporting and testing new technology.

**Figure 2: Unit 3 Makeup Water Treatment System**

**Makeup System Design**

The raw water supply, analysis shown in Table 1, originates from Lake Konomoc and is treated by the city of New London. Unit 3’s 200 gpm (0.8 m\textsuperscript{3}/h) makeup water treatment system is shown in Figure 2 with a 100 gpm (0.4 m\textsuperscript{3}/h) GTM unit incorporated. A by-pass is utilized during 200 gpm (0.8 m/h) peak demand periods. With the GTM, the makeup system utilizes three separate membrane processes. Each membrane unit has a separate operating purpose that complements the other. The makeup system, as originally designed, includes ultrafiltration (UF) followed by reverse osmosis (RO). The makeup water is then deoxygenated and polished by ion exchange demineralization.

**Table 1: Millstone Municipal Raw Water Supply**

<table>
<thead>
<tr>
<th>Cations (mg/l as CaCO\textsubscript{3})</th>
<th>Anions (mg/l as CaCO\textsubscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca\textsuperscript{2+}</td>
<td>0 - 30</td>
</tr>
<tr>
<td>Mg\textsuperscript{2+}</td>
<td>3 - 5</td>
</tr>
<tr>
<td>Na\textsuperscript{+}</td>
<td>8 - 16</td>
</tr>
<tr>
<td>K\textsuperscript{+}</td>
<td>1 - 2</td>
</tr>
<tr>
<td>CO\textsubscript{2} as CO\textsubscript{2}</td>
<td>45 - 65 mg/l</td>
</tr>
<tr>
<td>SO\textsubscript{4} as SO\textsubscript{4}</td>
<td>0.75 - 1.5 mg/l</td>
</tr>
<tr>
<td>pH</td>
<td>6.1 - 8.1</td>
</tr>
<tr>
<td>Conductivity</td>
<td>50 - 90 \muhos</td>
</tr>
<tr>
<td>TOC as C</td>
<td>2 - 6 mg/l</td>
</tr>
<tr>
<td>Turbidity</td>
<td>0.01 - 2.0 NTU</td>
</tr>
</tbody>
</table>

**Ultrafiltration**

The UF utilizes an 80,000 molecular weight cut off polysulfone membrane in a hollow fiber configuration. The system, operating between 85% to 90% recovery, effectively pretreats the city supply to minimize colloidal fouling on the downstream RO membranes. The UF membranes are chemically cleaned on a daily to monthly basis depending on the city water quality. Cleaning requirement is determined by effluent silt density index greater than five, increasing pressure drop or flux decline.

**Reverse Osmosis**

The RO utilizes cellulose acetate (CA) membranes in a spiral wound configuration. Cellulose acetate membranes, on this water supply, have successfully demonstrated nine years operating experience without a single cleaning.

This membrane process reduces the total dissolved solids (TDS) loading on the downstream ion exchange demineralizer by 85% to 95%. A typical permeate analysis is tabulated in Table 2. Chemical pretreatment to the RO includes chlorine for
biological control and sulfuric acid to prevent CA membrane hydrolysis.

### Table 2: RO Permeate Quality

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDS as ions</td>
<td>5 - 7 mg/l</td>
</tr>
<tr>
<td>Conductivity</td>
<td>5 - 13 μmhos</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>&lt; 1.0 mg/l</td>
</tr>
<tr>
<td>CO₂ as CO₂</td>
<td>6 - 12 mg/l</td>
</tr>
<tr>
<td>O₂ as O₂</td>
<td>5 - 8 mg/l</td>
</tr>
<tr>
<td>TOC as C</td>
<td>0.2 - 0.4 mg/l</td>
</tr>
<tr>
<td>pH</td>
<td>6.1 - 8.1</td>
</tr>
</tbody>
</table>

On higher hardness and alkaline feeds, acid pretreatment reduces the Langlier Saturation Index (LSI) in the RO reject stream, preventing calcium carbonate membrane scaling. Although injecting acid minimizes CA membrane hydrolysis and reduces the scaling potential, it creates free carbon dioxide, refer to Eq. (1).

#### Equation 1

\[
\text{H}_2\text{SO}_4 + \text{Ca} (\text{HCO}_3)^- \leftrightarrow \text{CaSO}_4 + 2\text{H}_2\text{O} + 2\text{CO}_2
\]

Every 1 ppm H₂SO₄ added to the RO feed increases the CO₂ concentration by 0.89 ppm. Reverse osmosis membranes do not remove dissolved gases. Therefore, the RO permeate contains equal amounts of CO₂ as generated in the feed water, adding undue ion exchange loading on the down stream demineralizer. Conventionally, CO₂ is removed by forced draft aeration or vacuum deaerators.

#### Deoxygenation

The RO permeate is deoxygenated to less than 3 ppb dissolved oxygen utilizing a patented DEOX* process. The process, catalyzed by activated carbon, reacts dissolved oxygen with hydrazine producing nitrogen and water. Hydrazine over feed and carbon leachables are removed by the down stream ion exchange demineralizer.

#### Demineralization

Demineralization and removal of carbon leachables is accomplished by a three step ion exchange process employing strong acid cation, strong base anion and polishing mixed bed resin. The activated carbon for the DEOX process and the ion exchange demineralizer are mobile mounted for off site regeneration. The final effluent quality is tabulated in Table 3.

### Table 3: Makeup Water Quality

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity</td>
<td>0.056 μmhos</td>
</tr>
<tr>
<td>Silica as SiO₂</td>
<td>&lt; 5 ppb</td>
</tr>
<tr>
<td>Na⁺ as ion</td>
<td>&lt; 0.2 ppb</td>
</tr>
<tr>
<td>Cl⁻ as ion</td>
<td>&lt; 0.1 ppb</td>
</tr>
<tr>
<td>O₂ as O₂</td>
<td>&lt; 3 ppb</td>
</tr>
<tr>
<td>TOC as C</td>
<td>&lt; 10 ppb</td>
</tr>
</tbody>
</table>

#### Gas Transfer Membrane

The GTM is piped in between the RO and the DEOX process. RO pretreatment is recommended to prevent fouling by colloids and large particles that might otherwise become entrapped in the GTM’s hollow fibers. Originally designed, the makeup system removes the CO₂ generated in the RO process only by the strong base anion exchange resin in the demineralization process.

Selecting Unit 3’s makeup system for the test site was based on the GTM’s CO₂ and O₂ removal capabilities. The test objectives for the study are:

- Carbon dioxide reduction.
- Dissolved oxygen reduction.
- Reduce hydrazine usage.

#### Results

During a four month period approximately two hundred data points were collected at varying feed pH, temperature and vacuum/nitrogen combinations. Over 2.5 million gallons (9500 m³) were treated during the GTM test. As illustrated in Figure 3, oxygen removal ranged between 78% and 95%. Carbon dioxide removal, illustrated in Figure 4, ranged from 65% to 95%.
The GTM influent and effluent CO\textsubscript{2} concentration at this site is below the detectable 10 ppm wet chemistry method employed. The CO\textsubscript{2} data presented here is calculated using standard methods\textsuperscript{13} and weak acid chemistry. Based on stoichiometric acid feed, the maximum calculated CO\textsubscript{2} concentration feeding the GTM unit is 6 to 12 ppm. Based on the 65% to 95% CO\textsubscript{2} removal efficiency, this equates to 0.3 ppm to 4.2 ppm GTM effluent CO\textsubscript{2} concentration. Carbon dioxide concentration depends on the chemical relationship between alkalinity and pH, refer to Eq. (7).

**Equation 7**

\[
\text{pH} = pK1 + \log \left( \frac{[\text{HCO}_3^-]}{[\text{CO}_2]} \right)
\]

where: \(pK1 = -\log\) of dissociation constant

\([\text{HCO}_3^-]\) = bicarbonate concentration (moles/l)

\([\text{CO}_2]\) = carbon dioxide concentration (moles/l)

Based on this relationship, Equation (7) is solved for \([\text{CO}_2]\), providing a method where by carbon dioxide concentration is calculated, refer to Eq. (8).

**Equation 8**

\[
[\text{CO}_2] = \frac{10^{10.5}}{K_c} \times [\text{HCO}_3^-]
\]

The GTM’s dissolved gas removal efficiency, expressed as a percentage, is defined by Equation (9).

**Equation 9**

\[
\% \text{ Removal} = \left(1 - \frac{\text{Gas (EFF)}}{\text{Gas (INF)}}\right) \times 100
\]

Assuming the alkalinity concentration does not change through the GTM unit, combining Equation (8) and (9) calculates removal efficiency based on the influent (INF) and effluent (EFF) pH change, refer to Eq. (10).

**Equation 10**

\[
\% \text{ Removal} = \left[ 1 - \left( \frac{10^{\text{INF pH}}}{10^{\text{EFF pH}}} \right) \right] \times 100
\]

Based on these equations, pre and post in-line pH probes were installed to measure the pH difference across the GTM. This allowed for a reliable in-line method to monitor CO\textsubscript{2} removal performance. Figure 5 illustrates that CO\textsubscript{2} removal efficiency is linearly related to feed pH. At lower pH with correspondingly higher feed CO\textsubscript{2} concentrations, percent removal exceeds 85%. This data, when extrapolated, shows that optimum operating pH for CO\textsubscript{2} removal is 4.7 (free mineral acidity) where all alkalinity is converted to CO\textsubscript{2}. The data was collected at 70°F to 72°F (21°C to 22°C) and vacuum at 27” Hg.

**Figure 5: Carbon Dioxide Removal pH Effect**
Figure 6 demonstrates CO₂ removal efficiency versus temperature. Carbon dioxide removal improves as the feed water temperature increases. As the water temperature approaches its boiling point, gas removal approaches 100%. As water temperature approaches its freezing point, gas removal approaches 0%. This data was collected at influent pH 5.0 to 5.5 and vacuum at 27” Hg.

**O₂ Removal**
Oxygen solubility is not dependent on pH changes. Hence, oxygen removal is easier to understand and accomplish than CO₂.

During the test dissolved oxygen data was collected at varying temperatures and while applying nitrogen sweep gas with and without vacuum. The GTM consistently reduced the dissolved oxygen below 1.1 ppm. The minimum dissolved oxygen concentration recorded was 350 ppb utilizing nitrogen and vacuum. Utilizing vacuum only, dissolved oxygen concentration ranged between 900 to 700 ppb. In addition to varying conditions, the GTM's effect on the hydrazine usage for the downstream deoxygenation process was investigated. Figure 8 illustrates the logarithmic temperature effect on the GTM's dissolved oxygen removal. This information is reported in a semi-log format so that the relationship can be shown linearly. As expected, dissolved oxygen removal efficiency improves with increasing temperature. Over a 55°F to 77°F (13°C to 25°C) temperature range, the GTM’s effluent dissolved O₂ decreased from 1.3 ppm to 0.6 ppm respectively.
Catalyzed oxygen removal processes reduce dissolved oxygen by greater than 99.9%. The patented deoxygenation system permanently installed in the plants make-up system achieves less than 3 ppb dissolved oxygen. Installing GTM, prior to the catalyzed oxygen removal process, dropped hydrazine consumption 7 to 10 fold without sacrificing dissolved O2 effluent quality. The data illustrated in Figure 10 reveals a substantially reduced hydrazine requirement. Combining these processes includes several advantages:

- Minimizes hydrazine handling.
- Reduces hydrazine consumption.
- Reduces TDS loading on down stream demineralizer due to excess hydrazine over feed.
- Provides efficient means to produce < 3 ppb dissolved O2 utilizing a two step process.
- Provides system redundancy.
- Does not increase operation requirements.

In order to achieve less than 3 ppb dissolved O2 with GTM alone, multiple units in series, combined with vacuum and nitrogen sweep gas is suggested. GTM and catalytic oxygen removal systems have site specific evaluated costs. Working in combination, single pass GTM with a catalytic oxygen removal system down stream significantly reduces operating and equipment cost for both processes.

**Conclusion**

This study provides insight into dissolved oxygen and low level carbon dioxide removal utilizing a new membrane process. GTM technology offers several advantages over conventional dissolved gas removal methods. GTM’s are comparably smaller, modular in design and offer lower capital cost with no chemical requirements.

Operating several GTM units in series with and without nitrogen sweep gas is a subject for future reports. Furthermore, higher CO2 feed concentrations warrant investigation. And, additional testing is required for a proper cost analysis versus achievable effluent quality. The data presented here provides a strong foundation for GTM technology that can be used to design future makeup water treatment systems.

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references


