Because salt and other small components are the most common compounds in wastewater from the process industry, desalination techniques are likely to be suitable as treatment processes in many cases. Although membrane distillation (MD) is a well-known technology for desalination and water treatment, it is not yet applied in industry. Membrane distillation differs from other membrane technologies in that the driving force for desalination is the difference in vapor pressure of water across the membrane, rather than total pressure. The membranes for MD are microporous and hydrophobic, which allows water vapor (but not liquid water) to pass. The vapor pressure gradient is created by heating the source water, thereby elevating its vapor pressure.

The major energy requirement of MD is low-grade thermal energy. It is expected that the total costs for water purification with membrane distillation will be lower than $0.50/m³, even as low as $0.26/m³, depending on the source of the thermal energy required for the evaporation of water across the membrane. Because low-grade heat is readily available in industry, MD can very well be applied for desalination of process streams.

The costs of the incoming water will probably increase in the future and the sources will be limited, such as the use of groundwater for industrial purposes. Also, the costs of the wastewater produced will increase as a result of more stringent limits for discharge, both in quantity and in quality. Often, additional treatment facilities are required because of site expansion and/or tighter environmental regulations. Water is generally seen as cheap, nonhazardous, and safe and, therefore, process engineers are often not fully aware of water issues and the costs of misusing water are not well understood. The water use in industry can be classified in two groups: low-value applications, such as rinsing and cooling water, and high-value applications, such as process water, product water, drinking water, and demineralized water.

Dedicated process water treatment facilities require high capital costs without any return on investment, and savings in the water bill alone are unlikely to justify investment in recycling or reusing water, although we rarely account for the full benefits of water recycling.
Reduced capital for the WWT plant
Greater WWT plant capacity
Simpler technology for WWT
Meeting discharge consents reliably
Product and raw material recovery
Improved company image
Reduced failures, maintenance, and downtime
Increased plant capacities

To reuse or recycle process water, an inventory must be carried out of the available process streams and of the composition of those streams. Also, the requirements for reuse of water must be known and whether specific compounds must be removed or recovered. More often than not, the quantity and quality of the process streams are unknown, just as the requirements for reuse. If, however, the quantity and quality of the available process streams for reuse and the requirements for the treated water are known, then a suitable regeneration process can be chosen either in a process-integrated solution or as an end-of-pipe solution. The situation after the inventory of the available process streams was taken, and after the actions arising from that were carried out, is depicted in Figure 2. The waste stream of process 1 is treated separately and is partially recycled. The waste stream from process 2 could be reused directly and the waste stream of process 3, which contains for instance spent catalyst, is treated separately and the discharge is fed to the central WWT plant. The boiler blowdown, the flow from the ion-exchange unit, and the cooling tower blowdown are discharged without any treatment, provided the discharge of salts is allowed. The condensate can easily be recycled after a minimal treatment.

2. EXISTING DESALINATION TECHNOLOGIES

Current commercially available desalination technologies can be subdivided in thermal processes, which evaporate water, while the salt remains in the brine, and membrane processes, which use a membrane as separating agent.

Reverse osmosis (RO) is a well-established unit operation, which is used both for treatment of raw water and for regeneration of wastewater [1]. It is a pressure-driven process and the applied pressures are depen-
dent on the salt content of the feed because the osmotic pressure must be overcome [2]. The membranes are hydrophilic and are tight, with pore sizes < 0.002 μm. Because of the tight membranes and the osmotic pressure, the feed pressure for treating salt (sea) water is between 40 and 80 bar, for brackish water between 15 and 25 bar, and for water with a low salt content about 5 to 10 bar. Because concentration polarization and scaling can dramatically decrease the flux through the membrane, an extensive pretreatment is required. The requirement for the feed for a RO installation is an SDI (silt density index) < 3. The permeate quality is dependent on the membrane characteristics.

Membrane distillation is an emerging technology that can be used not only for desalination but also for recycling [3]. Membrane distillation differs from other membrane technologies in that the driving force for desalination is the difference in vapor pressure of water across the membrane, rather than total pressure. The membranes for MD are microporous (pore size 0.05–0.2 μm) and hydrophobic, which allows diffusion of water vapor, but not of liquid water. Concentration polarization does not play a role in MD because fluxes are limited by temperature polarization. An extensive pretreatment like that for RO is thus not required. The feed quality can have an SDI as high as 100, but compounds that make the membranes hydrophilic, such as surfactants and volatiles that are not wanted in the permeate, must be absent. The vapor pressure gradient is created by heating the source water, thereby elevating its vapor pressure.

3. MEMBRANE DISTILLATION CONFIGURATIONS

A variety of methods have been used to impose the vapor pressure difference across the hydrophobic membranes [3], leading to different configurations as depicted in Figure 3. In every case, the raw water to be desalted directly contacts the hot side of the membrane. The solution does not penetrate into the membrane pores, which is called membrane wetting, because of the hydrophobic nature of the membrane. The function of the membrane is to support a liquid–vapor interface; the membrane does not alter the vapor–liquid equilibrium. The driving force for mass transport across the membrane is a difference in partial vapor pressure of the moving species. The way in which this partial vapor pressure difference is created differs for every MD configuration, as will be explained with the help of Figure 3.

3.1. Direct Contact MD

In direct contact MD (Figure 3a), the membrane is in direct contact with the feed solution on one side of the membrane and with the permeate on the other side. The temperature of the feed solution is higher than that of the permeate solution, to create a driving force for vapor transport across the membrane. Because the membrane is the only barrier between both solutions, the obtained water vapor fluxes in direct contact MD are relatively high. Unfortunately, this is also true for the energy flux by heat conduction, so that heat losses in direct contact MD are also relatively high.

3.2. Air Gap MD

In air gap MD (AGMD; Figure 3b), only the feed solution is in direct contact with the membrane. The permeate is condensed on a cold surface. There is an air gap situated between the membrane and the cold surface to reduce energy loss by heat conduction through the membrane. The main drawback of the air gap is that it is also an additional resistance to mass transfer. Air gap MD is suitable for all direct contact MD applications. However, it is also suitable for separating other volatile substances such as alcohols from an aqueous solution [5, 6]. This is not possible in direct contact MD because those substances are likely to wet the membrane at the permeate side as a result of a lower surface tension and/or smaller contact angle with the membrane. Because in air gap MD the permeate is not in direct contact with the membrane there is no danger of membrane wetting at the permeate side in this case.

3.3. Sweep Gas MD

In sweep gas MD (Figure 3c), which is also called membrane airstripping, the vapor at the permeate side of the membrane is removed by a sweep gas and subsequently externally condensed. Like air gap MD, it can also be used for removing volatile substances other than water [7]. An advantage of using a sweep gas is that the resistance to mass transfer of the air gap is
substantially reduced. However, the drawback is the dilution of the vapor by the sweep gas, which leads to higher demands on the condenser capacity.

3.4. Vacuum MD

Instead of using sweep gas the vapor can also be removed by evacuation (Figure 3d) and subsequent external condensation. Vacuum MD can be used for the separation of various aqueous mixtures with volatile compounds [10–12], and recently it has also been proposed as a means for seawater desalination [13].

3.5. Memstill® Concept

The Memstill® concept was developed by TNO, a scientific institution in The Netherlands, for desalination of seawater by air gap membrane distillation carried out in a countercurrent flow configuration. A schematic presentation of the technique is given in Figure 4. Cold seawater flows through a condenser with nonpermeable well-wettable walls by a heat exchanger into the membrane evaporator in countercurrent mode. The wall of the evaporator consists of a microporous hydrophobic membrane through which water vapor can diffuse and by which liquid water (with dissolved salts) is retained. The condenser and the membrane can either be tubular, as shown in Figure 4, or can consist of flat sheets with spacers between the sheets.

The Memstill® concept can best be classified as air gap MD (Figure 3b), in which the cold surface is cooled by the feed flow that is preheated by the condensing water vapor. As noted earlier, a drawback of this configuration is the resistance to mass transfer of the air gap. Reduction of air gap width or air gap pressure, or both, will lead to a reduction of this resistance to mass transfer. Reduction of the air gap pressure does not mean that the process becomes a vacuum MD process because the objective remains to condense the product water inside the module at the highest possible temperature.

4. DRIVING FORCE: TEMPERATURE DIFFERENCE AND TEMPERATURE LEVEL

In the AGMD process, the applied driving force is the temperature difference between the hot and the cold water flow. The direct driving force that makes the water molecules diffuse across membrane and air gap is the water vapor pressure difference between the hot water surface at the inner membrane radius and the condenser layer surface. At both surfaces local vapor–liquid equilibrium is assumed [3]. As can be seen in Figure 5, the saturated water vapor pressure increases exponentially with temperature. This means that a given temperature difference results in a larger flux with increasing hot water temperature. For example, a temperature difference of 10° C at hot water temperatures of 80 and 40° C results in vapor pressure differences of, respectively, 162 and 31 mbar, differing by a factor of five. The production of water vapor is thus much more efficient at higher temperatures, as can be seen in Figure 6.

5. HEAT AND MASS TRANSPORT

In MD processes, mass transport and energy transport are coupled. Water evaporates from the hot water flow, before it diffuses across membrane and air gap. When reaching the other side of the air gap, the water vapor condenses on the cold surface. The heat of evaporation must be supplied from the hot water bulk to the hot water–membrane interface, and heat of evaporation must be withdrawn from the condenser layer by the cold feed flow.

Because a larger energy flux increases the tempera-
ture difference between the hot water bulk and the evaporating surface and between the condensing surface and the cold water bulk, it leads to a smaller net driving temperature difference between the evaporating and condensing water surfaces. This phenomenon is often called temperature polarization in membrane science and it reduces the water vapor flux. Thus, next to temperature level and temperature difference, the water vapor flux is also influenced by the horizontal energy flux across the module, which consists of latent energy of evaporation, which is coupled to the water vapor flux, and also of heat conduction.

Energy transport by heat conduction, which forms the other part of the energy flux, is especially important in direct contact MD. The negative influence of conductive energy loss is twofold: (1) the energy is lost for evaporation of water and (2) it leads to extra temperature polarization because of the increased energy flux. This is why the use of an air gap to reduce energy loss can be so advantageous. Several studies show theoretically possible efficiencies of air gap MD between 80 and 95% [14–16].

Description of the energy transport in a MD system is straightforward. If a steady state is assumed, the heat flow across all heat transfer resistances between the bulk at the feed and the permeate side will be constant. For the AGMD process, these resistances are: the hot water boundary layer, the membrane, the air gap, the product layer, the cooling plate, and the cold water boundary layer.

The driving force for mass transfer across the membrane is the water vapor pressure difference between feed and permeate side. The recognized transport mechanisms for mass transfer across the membrane are usually molecular diffusion and Knudsen diffusion and, sometimes, viscous flow.

A useful theory for the AGMD case combines the transport mechanisms explicitly and has constant membrane parameters that do not depend on process conditions. Such a theory is the dusty-gas model [17–19], which has been introduced in the MD field by Lawson [20].

6. CURRENT STATE OF THE MEMSTILL® TECHNOLOGY

6.1. Air Gap Width

Memstill® technology research aims at maximizing flux per driving force by optimizing module configuration, including air gap width and spacer design, and process conditions, such as air gap pressure and operation schemes. Measurements with hollow-fiber membranes with variable air gap width (at a hot water entrance temperature of 65°C) show that, for air gaps of ≤1.5 mm, the energy efficiency of the process decreases with >20%. This is attributed to thermal conduction taking place across product water, which forms water bridges between the membrane and the condenser wall. For large air gaps of 3 mm energy efficiencies of typically 85–90% were obtained [19].

The highest fluxes are obtained at the lowest possible pressures in the air gap. This lowest pressure is equal to the saturated water vapor pressure of the hot water entering the module. At this pressure, the air gap width is of negligible influence on the water vapor flux.

6.2. Concentration Polarization

To minimize both concentration polarization and temperature polarization, research was carried out by applying different spacers in the membrane channel. Supersaturation profiles of barium sulfate are shown to be dependent on the inlet temperature of the membrane channel and, at certain conditions, a maximum value of the barium sulfate concentration lies in the bulk of the channel rather than at the membrane surface [21]. In Figure 7, the concentration profile of BaSO₄ in the membrane channel is shown at an inlet temperature of 95°C. From this figure, it is clear that the maximum supersaturation of the salt is in the bulk, rather than at the membrane surface. At an inlet temperature of 80°C, however, the highest concentration of BaSO₄ is found at the membrane surface [21].

The use of spacers in the membrane channel substantially enhances the flux, as shown in Figure 8, and spacer 4, with a flow attack angle of 45° and an angle between the filaments of 90°, gives the highest flux [22].

![Figure 7](image_url). Supersaturation of BaSO₄ at T = 95°C, membrane at y = 0.01 m [21].
The description of the spacers used can be found in Table 1.

### 6.3. Biofouling

Biofouling is an issue when process water, waste-water, or surface water is being used as feed. In one laboratory plant (5 × 0.1 m² membrane area), with water from a pond as feed, a flux decline, especially in the segment with the highest temperature (57°C), was observed after 800 h as a result of biofouling, but no evidence of breakthrough of microorganisms was found with the membranes used. After 2200 h, the direction of the flow was reversed, which almost completely restored the original flux rate. Another lab installation (2 × 0.1 m² membrane area) was in operation elsewhere during 6000 h with surface water as feed, after pretreatment by coagulation/flocculation. In spite of severe biofouling of the membranes and partial clogging of some of the inlet channels (no prefilter was used), also here no evidence of bacterial breakthrough was observed.

### 6.4. Pilot-Plant Tests

Presently, pilot tests are being carried out with several modules up to a membrane area of 60 m². These pilot plants will be scaled up to 600 m² in the near future and pilot plants, with capacities ranging from 50 to 250 m³/day, will be installed in The Netherlands and in Singapore, where process (waste) water and salt water will be used as feed.

### 7. Potential of the Memstill® Technology

The energy consumption of the Memstill® is low (80–240 MJ/m³, depending on the top brine temperature) because in the Memstill® technology, low-grade heat, with a temperature of 50–100°C, or solar energy can be used to heat up the feed. Because Memstill® operates in countercurrent mode efficient use of the energy supplied is obtained. Also in comparison with RO, the energy consumption is low. RO requires electrical energy for the high-pressure pumps and MD uses heat only.

The Memstill® installation consists of prefabricated modules, which results in easy construction and minimal site work. Because the components are mainly made of polymeric materials, which are commercially available, the construction is lightweight and thus requires a light foundation and is easy to (re-)locate. Because of its properties, a Memstill® unit can easily be placed on ships and drilling platforms in the offshore industry for the production of drinking water from seawater. Because of the polymeric construction, corrosion plays only a limited role.

In MD, the driving force is a difference in vapor pressure on both sides of the membrane and this has the advantage that MD is less susceptible to fouling, compared to RO, where fouling and compaction of the fouling layer and the membrane are major drawbacks of this technology. The only pretreatment for MD is removal of solids out of the feed stream. Therefore, fewer chemicals and less pretreatment are required for MD than for RO.

Not only can Memstill® be applied in both small-scale and large-scale applications but it is also suitable for a number of applications, such as production of drinking or ultrapure water from surface water, brackish water or seawater, concentration of brines, and treatment of waste streams.

### Table 1. Description of spacers, thickness 4 mm, distance between filaments 14 mm [22].

<table>
<thead>
<tr>
<th>Spacer</th>
<th>Angle between filaments</th>
<th>Flow attack angle</th>
<th>Spacer type</th>
<th>Filament type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120</td>
<td>30</td>
<td>Nonwoven</td>
<td>Round</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>45</td>
<td>Nonwoven</td>
<td>Twisted tapes</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>45</td>
<td>Nonwoven</td>
<td>Round</td>
</tr>
<tr>
<td>4</td>
<td>90</td>
<td>45</td>
<td>Woven</td>
<td>Round</td>
</tr>
<tr>
<td>5</td>
<td>120</td>
<td>30</td>
<td>Nonwoven</td>
<td>Twisted tapes</td>
</tr>
</tbody>
</table>

**Figure 8.** Transmembrane flux as a function of Re [22].
8. COST COMPARISON
Because the results of the pilot-plant tests are not yet available, a comparison on costs of treatment processes in wastewater cannot be presented. Therefore, the present and expected costs for several desalination processes with seawater are shown in Table 2 and in Figure 9, from which it can be seen that the RO costs have decreased dramatically. The main reasons for this are the lower module costs, the development of energy-efficient RO membranes, and energy recovery systems, which recover about 50% of the energy required for RO. The costs of RO can be found in various reports in the literature [23–25]. The costs of MD were calculated by an engineering company within the Memstill consortium.

The process characteristics for the Memstill® process are:
- Specific flux: $J_s = 1.5 \times 10^{-10} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$
- Heat energy: 80–240 MJ/m$^3$
- Production: 25–50 m$^3$ day$^{-1}$ module$^{-1}$
- Recovery: 50%

Only in the case of a waste heat source, the energy costs of MD are at the same level or lower than those of RO. The hardware costs for MD are much lower than those for RO, mainly because for MD no high-pressure pumps are required. On the other hand, the costs for MD modules are higher because of the separate membrane and condenser compartments and because the flux rates are lower, although the total fixed costs for Memstill® are $0.16–0.17/m^3$, compared to $0.25–0.35/m^3$ for RO. Also, the cost for cleaning of the membranes is higher for MD than for RO. The lowest total costs of the water produced are obtained with a Memstill® installation with a cheap waste heat source of $0.10/GJ$.

9. CONCLUSIONS
Air gap membrane distillation is a promising desalination process because it is the most efficient MD process. Because a continuum of evaporative stages in an almost ideal countercurrent flow process occurs in a Memstill® module, a very high recovery of evaporation heat is possible.

Both sweet (surface or waste) water and salt water can be used as feed for the Memstill® module. No breakthrough of microorganisms was found during a test of 6000 h with pretreated surface water as feed.

With waste heat as an energy source, the total water costs with the Memstill® process can be as low as $0.26/m^3$. The lowest costs of other desalination processes (RO) are at least $0.45/m^3$.

AGMD is suitable for applications in wastewater treatment in the chemical process industry because of the use of waste heat as a cheap energy source and because of the low requirements for pretreatment of the feed to the MD installation.

The Memstill® technology is in operation only on the pilot-plant scale and thus must still be proven on a larger scale.
LITERATURE CITED