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Membrane Engineering for Green Process Engineering

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ABSTRACT

Green process engineering, which is based on the principles of the process intensification strategy, can provide an important contribution toward achieving industrial sustainable development. Green process engineering refers to innovative equipment and process methods that are expected to bring about substantial improvements in chemical and any other manufacturing and processing aspects. It includes decreasing production costs, equipment size, energy consumption, and waste generation, and improving remote control, information fluxes, and process flexibility. Membrane-based technology assists in the pursuit of these principles, and the potential of membrane operations has been widely recognized in the last few years. This work starts by presenting an overview of the membrane operations that are utilized in water treatment and in the production of energy and raw materials. Next, it describes the potential advantages of innovative membrane-based integrated systems. A case study on an integrated membrane system (IMS) for seawater desalination coupled with raw materials production is presented. The aim of this work is to show how membrane systems can contribute to the realization of the goals of zero liquid discharge (ZLD), total raw materials utilization, and low energy consumption.

1. Introduction

In the early 1960s, Loeb and Sourirajan fine-tuned an effective method for significantly increasing the permeation flux of polymeric membranes without significant changes in selectivity. Their work in the preparation of asymmetric reverse osmosis (RO) membranes initiated industrial interest in membranes. Today, RO is a well-recognized basic unit operation. In fact, according to the last report of the International Desalination Association (IDA) [1], around 80% of desalination plants currently use RO as their separation technology. This technology is successful because it has the highest water recovery factor, lowest energy consumption, and lowest water cost of any conventional process. The intrinsic properties of membrane operations make them ideal for industrial production: They are easy to scale up, modular, and generally athermal; they do not involve phase changes or chemical additives; and they usually have low energy consumption, the potential for more rational utilization of raw materials, and the potential for the recovery and reuse of byproducts. For these reasons, membrane engineering meets the requirements of green process engineering toward the realization of sustainable industrial development. Moreover, the integration of different membrane operations in the same industrial cycle can lead to further important benefits in terms of product quality, plant compactness, environmental impact, and energy use.

This paper discusses some of the main membrane-based technologies that are employed in water treatment, blue energy production, raw materials exploitation and reuse, crystallization, and condensation. It also presents a case study on an integrated membrane system (IMS) for seawater desalination coupled with raw material production.

2. Current limitations

Energy supply, potable water availability, raw material depletion,

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and environmental protection are the foundations for sustainable development in every society. Potable water production has become a worldwide concern; for many communities, the projected population growth and associated demand exceed conventionally available water resources. A large part of the global population lacks access to potable water and sanitation; this lack is a major source of disease and an obstacle to sustainable growth. Indeed, the sustainable provision of clean water resources is important to all economies, irrespective of size. Crop irrigation, product manufacturing, and refining for biofuels may place further significant demands on water resources [2]. Possible measures to alleviate water problems include the repair of water infrastructure, improved catchment and distribution systems, wastewater treatment and reuse, and desalination. The last of these options offers one of the most important solutions to problems of water availability.

Mineral deficiency is also becoming quite common all over the world in recent years. For example, lithium demand has doubled over the past decade, and evaluations indicate higher lithium consumption in the future. The demand for uranium (as an energy source) has already exceeded global production, and is projected to increase from 61 500 t in 1997 to 75 000 t in 2020 [3]. In addition, estimates indicate that other compounds such as antimony, indium, silver, and zinc will be used up within the next 46 years if consumption continues at the current rate, and within 30 years if the demand for them grows.

Energy consumption has grown rapidly in recent decades, and is projected to increase further (Fig. 1). Moreover, environmental protection and water/energy/raw material demand are strongly interconnected. An example can be found in electric power plants, which consume vast amounts of water in cooling circuits. The oil and gas industry also consumes water and produces large quantities of waste and polluted water. The terms "oilfield-produced water" or "produced water" are used in the oil and gas industry to refer to the wastewater that forms as a byproduct.

Produced water may be ① water that is injected into the reservoir to enhance oil recovery, which is the main source of wastewater; ② the flow of back water from hydraulic fracturing activities; and ③ a mixture of both [4]. Produced water contains various organic and inorganic fractions, including dissolved and dispersed oil compounds, dissolved minerals, production chemical compounds, production solids, and dissolved gases. This wastewater can cause the pollution of surface and ground waters and can pose a serious environmental threat.

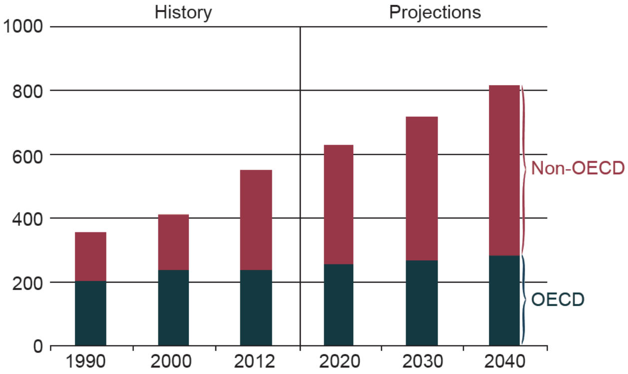

Fig. 1. World energy consumption, 1990–2040. The unit for the *y*-axis is quadrillion Btu (1 Btu = 1.05506 × 10^3 J). OECD refers to all members of the Organization for Economic Cooperation and Development, and non-OECD refers to nations outside of the Organization for Economic Cooperation and Development.[†]

On the other hand, the treatment and reuse of produced water and the production of water via desalination involve energy utilization. Energy is required for different steps of water production, from water intake to freshwater separation and distribution. Gude [5] reports that the production of 1000 t (m^3) per day of freshwater by means of desalination technologies requires 10 000 t of oil per year, and results in environmental degradation through greenhouse gas (GHG) emissions and brine discharges. Phrases such as "oil for water" or "water for non-renewable energy" are used to describe this situation; water is also being called "the new oil." These phrases refer to the current pressing demand on the exhaustible fossil fuel reserves around the world—a situation that creates social and economic impacts [5].

In addition to these issues, the use of desalination carries serious concerns regarding potential environmental impact. In fact, although desalination plants produce large volumes of desalted water, they also produce almost the same amount of concentrate (i.e., brine). Brine-disposal costs represent 5%–33% of the total desalination cost [6], depending on the disposal treatment process and brine concentration. Moreover, the brine-disposal costs of inland plants are higher than those of coastal plants.

However, brine-disposal problems encourage the development of technologies that address brine exploitation. Examples include renewable energy generation, the use of salts for production, and the use of chemicals for industry. Seawater is around 96.7% water; the remaining 3.3% is composed of dissolved salts. These salts comprise all the elements of the periodic table from hydrogen to uranium; moreover, sodium (Na), magnesium (Mg), calcium (Ca), potassium (K), chlorine (Cl), sulfur (S), and bromine (Br) constitute around 93.5% of all the dissolved salts. At present, only a small quantity of chemicals is obtained from dissolved salts (mostly Na). However, various other components can be extracted, provided the elements are sufficiently valuable or rare on land to make the cost of extraction worthwhile.

This paper analyzes current and emerging membrane-based technologies for water extraction, energy production, and raw material production. It also highlights the benefits of membranes as compared with conventional processes and suggests future prospects and research trends.

3. Membrane engineering success and sustainability in various industrial sectors

3.1. Membrane-based desalination systems

Due to increasing freshwater scarcity, the practice of seawater desalination is rapidly increasing. Desalination technologies are categorized as thermal (phase-change) or membrane desalination, and these categories are further divided into subgroups. The main thermal desalination technologies include multistage flash (MSF), multi-effect distillation (MED), and vapor compression (VC); the main membrane-based technologies include RO, electrodialysis (ED), and electrodialysis reversal (EDR). Although thermal desalination technologies still exist and are mature, interest has shifted to membrane-based technologies in the last few decades, because of their more favorable energetics (i.e., lower specific energy consumption ($kWh\cdot m^{-3}$)). Seawater reverse osmosis (SWRO) is presently considered to be a conventional membrane-based technology. According to the IDA [1], in the first half of 2016, the global contracted capacity of desalination plants was 9.559 × 10^7 $m^3\cdot d^{-1}$, and the global online capacity was 8.856 × 10^7 $m^3\cdot d^{-1}$—a total increase of 2.1 × 10^6 $m^3\cdot d^{-1}$

[†] US Energy Information Administration, International Energy Outlook, 2016. May 11, 2016. Report Number: DOE/EIA-0484(2016). Available online: https://www.eia.gov/outlooks/ieo/world.cfm.

in new desalination capacity over 2015. As a parallel metric of growth, the proportion of large-scale seawater projects (i.e., those with a capacity above 50 000 $\text{m}^3\cdot\text{d}^{-1}$) has also increased from 6% to 12%, from 2015 to the first half of 2016. The largest regional gains occurred in the Middle East and in North Africa countries, driven by several large-scale seawater projects in multiple countries across these regions. For several countries in these regions, water demand outweighs the economic toll of persistently low oil prices. The general trend in technology is the adoption of membrane over thermal desalination technologies, a shift that became more acute from 2000 to 2016 (Fig. 2).

The widespread use of RO desalination plants is due to their lower capital costs, as they use less-expensive construction materials; their versatility in feed-water and application; and their stabilization of the price of produced desalted water. In the traditional thermal Middle East desalination market, thermal desalination technologies continued to dominate through the investment boom up to 2010. This was due to a lack of incentive to change, and also because the operators knew how to build and operate thermal desalination technologies that could desalinate the warm waters of the Gulf. Those drivers, however, have changed due to global recession and the subsequent decline of the thermal markets. The future capacity is expected to be largely membrane based [7].

However, SWRO is still an energy-intensive technology with associated GHG emissions and other environmental impacts (e.g., organism impingement/entrainment at intakes and brine disposal at outfalls). Thus, there is an interest both in the greening of SWRO and in emerging technologies that go beyond SWRO.

The specific energy consumption of SWRO has been significantly reduced from 5–10 $\text{kWh}\cdot\text{m}^{-3}$ to its present consumption of 3–4 $\text{kWh}\cdot\text{m}^{-3}$ (Table 1). It emits 1.4–3.6 kg CO_2 per cubic meter of produced water ($\text{kg}_{\text{CO}_2}\cdot\text{m}^{-3}$) [7–10], although this value strongly depends on the fuel that is used to produce the electricity. Thermal desalination technologies are less efficient, and generally emit 8–20 $\text{kg}_{\text{CO}_2}\cdot\text{m}^{-3}$, with the exception of stand-alone MED, which emits 3.4 $\text{kg}_{\text{CO}_2}\cdot\text{m}^{-3}$ (Table 2) [10,11]. Although these numbers may appear small when viewed from a global perspective, they can be large from the perspective of regional grids and ecosystems. Preliminary estimates show a direct carbon footprint of about 1.2×10^8 t annually [11] for the worldwide electric energy consumption of the desalination capacity that was online in 2013 (which was equal to 7.92×10^7 $\text{m}^3\cdot\text{d}^{-1}$ [7]).

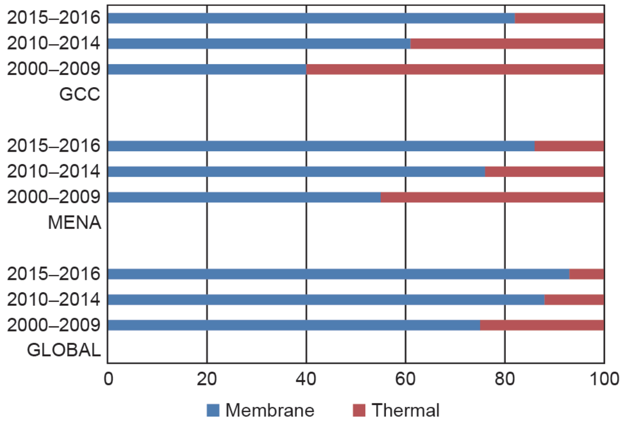

Fig. 2. Time evolution of membrane vs. thermal desalination technologies. GLOBAL: global situation; MENA: situation in Middle East and North African countries; GCC: situation in Gulf Cooperation Council countries.

Desalination can never be performed with zero energy usage. Elimelech and Phillip [12] estimate that the theoretical minimum energy of desalination for seawater with 35 000 ppm salt and a typical 50% recovery is 1.06 $\text{kWh}\cdot\text{m}^{-3}$. This value increases to 1.56 $\text{kWh}\cdot\text{m}^{-3}$ when the system has a finite size and is not operating as a reversible thermodynamic process, even if the operation occurs with ideal equipment (i.e., 100% efficient pumps and energy-recovery devices) and without concentration polarization or frictional losses [12]. Elimelech and Phillip [12] also report that the overall energy consumption of new SWRO plants is three to four times higher than the theoretical minimum energy, due to the need for extensive pre- and post-treatment steps. Therefore, for the further improvement of SWRO plants, future studies should focus on pre- and post-treatment. In fact, Zhu et al. [11] report that developing more-permeable membranes will not lead to substantial additional energy savings for a desalination process that is operating at the thermodynamic limit (i.e., when the applied pressure is equal to the osmotic pressure of the concentrate), but will only help in reducing capital costs by reducing the membrane area required. Moreover, high-permeability membranes are needed to solve the concentration polarization and membrane-fouling problems that are induced by the high water fluxes that are the weak point of current thin-film composite membrane modules [10].

Effective pre-treatment can affect the energetics of the RO step by reducing fouling. Dual media filtration (DMF) is the current conventional pre-treatment process [13]. However, IMSs with ultrafiltration (UF) pre-treatment, or UF-SWRO, are becoming more common [14], especially for waters that are difficult to treat. Both UF and dissolved air flotation (DAF) are receiving increasing attention for their potential resilience during “red tide” events (i.e., harmful algal blooms (HABs)), such as those experienced in the Gulf of Arabia [15].

Improvements in the pre-treatment of an SWRO process can also be realized with the development of: ① fouling-resistant membranes with tailored surface properties, which can resist the adhesion of a wide range of foulants; ② oxidant-resistant membranes, which can reduce the extent of pre-treatment; or ③ membrane modules with improved hydrodynamics conditions. Each of these techniques carries a specific challenge. Overall, there is a need to develop and use modified modules. Past experience in membrane operations has already showed that, after the initial phase, the membrane-production process and the related costs decrease, causing the membrane operations to become competitive with traditional

Table 1
Characteristics of recently constructed large-scale SWRO desalination plants.

	Total capacity ($\text{m}^3\cdot\text{d}^{-1}$)	Date commissioned	Recovery (%)	Energy consumption ($\text{kWh}\cdot\text{m}^{-3}$)	Feed-water TDS ($\text{mg}\cdot\text{L}^{-1}$)
Carlsbad Desalination Plant (San Diego County, US)	204 390	2015	50	< 2.3	34 500
Al Ghubrah Independent Water Project (Oman)	191 000	2015	38	3.2–4	45 000
Barka IWPP expansion (Oman)	56 780	7.5 MIGD in Oct 2015 10 MIGD in Nov 2015 12.5 MIGD in Feb 2016	40	4.2	43 000

TDS: total dissolved solids; MIGD: million imperial gallons per day; IWPP: Independent Water and Power Plant.

Table 2
Representative direct GHG footprint in $kg_{CO_2}\cdot m^{-3}$ of fresh water [10,11].

Desalination technologies	GHG emissions
Reverse osmosis	1.4–3.6
Multi-effect distillation with thermo-vapor compression	8–16
Multistage flash	10–20

manufacturing procedures. Further enhancements to the SWRO process are related to the increase of the water recovery factor, the improvement of water quality, and the reduction of the brine-disposal problem. As described in Sections 3.2 and 3.3, these aims can be realized by developing new and emerging operations (such as membrane distillation (MD) and membrane-assisted crystallization (MCr)).

Another possibility for reducing energy consumption (and fossil fuel dependence) is the coupling of renewable energies with desalination [16]. The three main renewable energy sources available are solar (photovoltaic and thermal), wind, and geothermal energy. Other renewable resources are hydroelectric, biomass, and ocean energy. These energy sources release little or no gaseous or liquid pollutants during operation, and offer many environmental benefits compared with conventional energy sources (such as reduced GHG emissions, reduced depletion of finite sources, and reduced dependence on the few global oil-exporting regions) [16]. Overall, the energy source that is most often used is solar energy (70% of the market), while RO covers the majority (62%) of the renewable energy desalination market [17]. The solar-SWRO plants that are currently in operation are small-scale plants, and most are only for demonstration; in total, they represent approximately 0.02% of the total world desalination capacity [18]. The largest solar-SWRO plant in the world (30 000 $m^3\cdot d^{-1}$) is under construction in Saudi Arabia. Although the use of renewable energy does not necessarily reduce specific energy consumption, it provides a reduction in GHG emissions. The interest in renewable energy is now evolving toward integrated systems and reaching beyond electricity-providing solar photovoltaic panels or wind turbines.

3.2. New and innovative technologies beyond SWRO

Several low-energy desalination technologies are emerging, including membrane-, thermal-, and electrochemical-based systems: ① *Membrane processes* include MD and forward osmosis (FO); ② *low-temperature thermal processes* include adsorption desalination (AD) and low-temperature distillation (LTD); and ③ *electrochemical desalination processes* include capacitive deionization (CDI) and membrane capacity deionization (MCDI). The following discussion focuses on the membrane-based processes: MD and FO.

MD is a thermal membrane separation process that involves the transport of vapor through microporous hydrophobic membranes. It operates on the principle of vapor-liquid equilibrium as a basis for molecular separation [16]. The driving force of the process is supplied by a partial pressure difference between the two sides of the membrane, which is caused by a temperature gradient imposed between the liquid-vapor interfaces [16].

One of the advantages of MD over conventional distillation technologies (i.e., MED and MSF) is its lower operating temperature, which permits the efficient use of low-grade or waste heat streams, or alternative energy sources (i.e., solar, wind, or geothermal). MD requires energy input in two forms: thermal (to drive the separation process) and electrical (to move feed, product, and brine flows). Villacorte et al. [15] report that the thermal power requirement is higher than 100 $kWh\cdot m^{-3}$, whereas only about 1.0 $kWh\cdot m^{-3}$ of electrical power is needed. Other key attributes of MD are that it is less prone to fouling than pressure-driven membranes, and that it has a small footprint. Moreover, as described below, there is an emerging interest in MD as part of a zero liquid discharge (ZLD) scheme for inland desalination. In this process, recovery is increased to approach crystallization, such that the process becomes MCr. The main requirement for MD and MCr membranes is that they be hydrophobic. A few microporous hydrophobic membrane materials, such as polypropylene (PP), polyvinylidene fluoride (PVDF), and polytetrafluoroethylene (PTFE), are available as hollow fibers and flat sheets; these materials have been used in MD experiments [19], although they were originally prepared for microfiltration (MF) or UF purposes [18,20]. Attention has recently been paid to manufacturing specific membranes for MD applications [21–23]. In fact, the desired properties of MD membranes are quite different than those of common separation membranes. MD membranes should be highly hydrophobic with a narrow pore size distribution, high porosity, and high resistance to liquid entry pressure.

FO is a membrane operation that can be used to remove dissolved components from water. FO exploits the osmotic pressure gradient across a semi-permeable membrane to promote a water flow from a feed solution into a concentrated draw solution. Next, the draw solution is treated in order to remove the clean water, and the draw solution is re-utilized. The energy consumption of FO is low because this process requires only the stirring or pumping of the solutions involved [16].

A problematic aspect of the FO process involves the external concentration polarization (ECP) and internal concentration polarization (ICP) phenomena. *Concentrative ECP* occurs when the feed solution flows onto the active membrane layer and the solutes build up on the active layer. *Dilutive ECP* is caused by the dilution of the draw solution at the permeate-membrane interface by the permeating water. Both concentrative and dilutive ECP phenomena reduce the effective osmotic driving force. Due to the lower hydraulic pressure, membrane fouling that is induced by ECP has milder effects on water flux in FO than in pressure-driven membrane processes [24]. McCutcheon et al. [24] show that ECP plays a minor role in osmotic-driven membrane processes, and is not the primary cause of the lower-than-expected water flux in such processes. *Concentrative ICP* is a phenomenon that is similar to concentrative ECP, except that it takes place within the porous layer; therefore, it cannot be minimized by cross-flow. *Dilutive ICP* is due to the dilution of the draw solution within the porous substructure by the permeating water. Various studies [25–27] have shown that ICP is the actual cause of substantial flux decline in FO. Important measures to advance the field of FO include the development of new flat-sheet and hollow-fiber membranes that can provide high water permeability, high solute rejection, substantially reduced ICP, high chemical stability, and high mechanical strength [24].

Significant progress has been made in the evolution of higher flux, lower salt leakage, commercially available FO membranes; one company recently commercialized an aquaporin FO membrane [15]. There has also been recent progress in developing hollow-fiber FO membranes [28]; a new prototype hollow-fiber FO membrane has shown a flux higher than 40 $L\cdot(m^2\cdot h)^{-1}$ against a draw solution of 2 $mol\cdot L^{-1}$ NaCl [29].

The discussion of emerging membrane-based processes can be extended from desalination to power generation. Power can usually be generated from salinity gradients by utilizing the technologies available for desalination but operating them in the reversed mode. Examples include pressure-retarded osmosis (PRO) and reverse electrodialysis (RED).

PRO, which is a variation of FO, can produce salinity gradient (blue) energy. In PRO, two solutions with different salinities are brought into contact through a semi-permeable membrane. The solvent (i.e., water) passes from the diluted solution to the concentrated solution due to the chemical potential difference between the two sides of the membrane. Hydrostatic pressure is applied to the concentrated solution to pressurize the volume of transported water [19]. The transported water is then used to generate electrical power in a turbine. Zhang and Chung [30] report that hollow-fiber PRO membranes can produce 24 $W{\cdot}m^{-2}$ at 20 bar (1 bar = 10^5 Pa). Sarp et al. [31] have calculated that an integrated PRO process can reduce the SWRO specific energy consumption by about 20% for a typical SWRO brine. The recent Mega-ton Water System project in Japan achieved a power density higher than 10 $W{\cdot}m^{-2}$ using a 7% SWRO brine in a demonstration-scale study with PRO membrane modules [32]. A PRO system using SWRO brine and wastewater reverse osmosis (WWRO) brine is being studied in Singapore [33], given that WWRO brine has no economic value.

RED is based on the transport of ions through a stack of cationic and anionic membranes. The compartments between the membranes are alternately filled with concentrated and diluted salt solutions. The salinity gradient results in a chemical potential difference over each membrane, causing ions to flow through the membranes from the concentrated solution to the diluted solution. The chemical potential difference over the electrodes can be used to generate electrical power by connecting an external load or energy consumer to the circuit [16].

Although salinity gradient power was recognized more than 50 years ago, many research and development issues—particularly issues related to membrane properties and costs—remain to be resolved before PRO and RED are available for large-scale commercial application [16]. However, the re-evaluation of these processes is advisable due to declining membrane costs, the increasing prices of fossil fuels, and the possibility of redesigning desalination plants for water and energy production via the integration of RO (a desalination technology) and RED (an energy production technology).

3.3. Existing and emerging concentrate minimization practices

As anticipated, RO partially satisfies the increasing water demand. However, as they operate with recovery factors that range from 30% to 85%, SWRO plants also generate a large volume of concentrated streams that contain the chemicals utilized in the pre-treatment along with all retained compounds. In addition, SWRO discharge containing RO brine constitutes a potentially serious threat to marine ecosystems. The concentrates generated from brackish water via a RO process (with 60%–85% recovery) have a concentration factor that is 2.5–7 times higher; the same is true for SWRO (with 30%–50% recovery), which results in a concentration factor that is 1.25–2.0 times higher [5]. The current practice when handling these concentrates is to discharge them into coastal waters; however, this practice can have detrimental effects on the aquatic life and coastal environment [5]. To mitigate major environmental concerns related to brine/concentrate discharges, concentrates should be pre-diluted with seawater to minimize the effects related to high salt concentrations [5]. Removing or recovering substances from the concentrates by implementing alternative treatment methods is an attractive option that offers both environmental benefits (by reducing the discharge) and economic profits (due to the extraction of valuable metals).

Many technologies have been developed for the recovery and reuse of brine. Concentrates treatment options can be classified into four groups, according to their final purpose [7]. The four types of treatment options are: ① technologies for the reduction and elimination of brine disposal, including solar evaporation, phytodesalination, evaporation and crystallization processes, MD, two-stage RO, closed-circuit desalination (CCD), seeded slurry precipitation and recycling, and FO; ② brine adaptation for industrial uses, including brine adaptation for the chlor-alkali industry and hydrochloric acid (HCl) and sodium hydroxide (NaOH) production using bipolar membrane electrodialysis; ③ technologies for commercial salt recovery, including the SAL-PROC process, zero discharge desalination, and integrated seawater desalination processes with either traditional crystallization or MCr systems; and ④ metal recovery.

Although the zero discharge of desalination brine involves very high treatment costs, various technologies are under development to minimize the effluent volume. For small plants in arid regions where land is available, solar evaporation is a suitable technology. Wind energy is utilized to evaporate brine from wetted surfaces in wind-aided intensified-evaporation (WAIV) technology. WAIV has reduced land requirements with respect to evaporation ponds. However, WAIV availability has been demonstrated only on a pre-commercial scale. Another technique in the experimental phase is phytodesalination. This technology permits brine reuse for irrigating soil or producing different crops. However, it can lead to soil and aquifer salinity. In contrast, concentrators and crystallizers, despite their high energy consumption, are developed at an industrial scale. Eutectic freeze crystallization (EFC) is a singular case that has been proposed by Fernández-Torres et al. [34] as an alternative to evaporative crystallization, which is energy-intensive and expensive. In EFC, the RO concentrate is continuously frozen until the eutectic temperature is reached. Heat removal beyond the eutectic temperature then results in both ice and salt crystallization. These ice crystals are washed and re-melted to obtain pure water. Although desalination by freezing has been proposed as a method for several decades, only a few pilot and demonstration projects have been conducted to date. Using EFC to treat RO concentrate (conductivity ~22 $mS{\cdot}cm^{-1}$), Randall et al. [35] demonstrated a 97% conversion of concentrate to pure water, with pure calcium sulfate ($CaSO_4$, 98.0% purity) and sodium sulfate (Na_2SO_4) salt products. Moreover, Fernández-Torres et al. [34] declared that EFC consumes 6–7 times less energy than evaporative crystallization in the case of mine wastewater treatment, for 4 wt% of Na_2SO_4 solution. In theory, freezing has other advantages over traditional desalination technologies as well, including fewer minor corrosion, precipitation, and incrustation problems. Its main disadvantage is the difficulty of handling ice, which is mechanically difficult to move and process [16].

As described above, MD allows the production of high-quality desalted water. MD has been developed at the industrial scale, despite its higher energy consumption compared with RO. One of the main advantages of MD is that it does not require extensive pre-treatment because it has fewer fouling problems than pressure-driven membrane operations. CCD is based on the recirculation of concentrate to the same RO membrane in a batch-like operation [36–38]. CCD achieves high recovery with reduced capital costs. However, permeate flow is lower for the same membrane area, which makes this configuration optimal for applications where capital costs are crucial and flow is not critical.

The utilization of seed crystals for the precipitation of $CaSO_4$ from RO concentrate has been evaluated to achieve more than 90% feed-water recovery for mine wastewater treatment applications, in a process called slurry precipitation and recycle reverse osmosis (SPARRO®) [39,40]. In this approach, seed crystals are introduced into a tubular RO membrane to precipitate the scaling of compounds onto the seeds. A slurry of seed crystals, which serve as nucleation sites, circulates within the RO system. Thus, $CaSO_4$ precipitates on the seed crystals instead of on the membrane surface. Concerns associated with the damage of membrane material by the seed crystals and plugging of the tubular membrane channels have resulted in marginal use of the SPARRO® process for concentrate treatment.

Two-stage RO and FO allow an increase in water recovery. In two-stage RO, the concentrate, which is at a first-stage RO working pressure, is pressurized before entering the second-stage RO modules. The main drawback of this process is the large amount of chemicals required. FO can result in highly concentrated brine and has low energy requirements compared with other membrane-based technologies; however, it requires draw solutes and specifically designed membranes to improve its performance.

The adaptation of brine for industrial uses involves complex processes to produce brine that is ready to feed an industrial plant [7]. Brine adaptation for the chlor-alkali industry requires a process for divalent cation removal from brine, followed by a technology such as electrodialysis for brine concentration. These treatments result in high costs that can be compensated for by the products obtained from electrodialysis. Chemicals such as NaOH and HCl can be obtained via bipolar membrane electrodialysis. However, this process is not applied at an industrial scale.

Processes for the recovery of commercial salts or the recovery of metals attract more interest than processes aimed only at treating effluents. It is undeniable that the former processes have high costs and are complex. However, salt and metal recovery can contribute to offsetting these costs. SAL-PROC is an integrated process aimed at achieving ZLD. It is designed for the sequential extraction of dissolved elements from inorganic saline waters via chemical precipitation reactions. Therefore, it requires chemical reagents such as calcium hydroxide ($Ca(OH)_2$) [41]. The SAL-PROC technology has been tested by Geo-Processors Inc. in field trials and pilots. This technology was used to recover salts from the concentrate of a multistage RO system during the treatment of coal-bed methane-produced water, in Queensland, Australia [42]. The SAL-PROC process is particularly recommended for brackish inland brines due to its high water recovery, and for brines with high concentrations of sulfate and potassium because of the high income that commercializing these salts can provide.

Curcio et al. [43] utilized MCr to minimize the brine-disposal problem and to recover salts and metals from seawater and from the brine streams of desalination plants. They claim that MCr can process streams until water and dry salts of high quality and controlled properties are obtained, thereby converting the traditional brine-disposal problem and cost into a new source of income. This system has multiple benefits: It avoids discharge to surface or ground waters, is flexible in site selection, and efficiently reuses water. Compared with conventional crystallization systems, MCr systems have important advantages such as a high interfacial area per volume unit, a low operating temperature and pressure, high rejection, a modular design, easy scale up, less membrane fouling, and low sensitivity to concentration polarization phenomena. Moreover, trans-membrane solvent evaporation, and hence the degree and rate of supersaturation, can be controlled very accurately depending on the process operating conditions (temperature, concentration, flowrate, etc.) and on the membrane characteristics (i.e., its chemical-physical properties). The effect is to control the nucleation and growth rate by choosing a broad set of available kinetic trajectories in the thermodynamic phase diagram, which are not readily achievable in conventional crystallization methods, and which lead to the production of specific crystalline morphologies and structures [44]. The drawbacks of this process are related to the presence of an additional mass transport resistance (the membrane itself) and to the rather limited range of operating pressures below the breakthrough threshold [45]. Its performance strongly depends on the properties of the membranes used. In general, a high hydrophobicity (for aqueous applications) is required to prevent wetting and mixing between the different phases in contact. Elevated permeability leads to high fluxes [45], and high chemical and thermal stability are necessary to improve the membrane resistance to chemical attack, degradation, and decomposition. Experimental evidence can be found in several published articles [46–48], demonstrating the possibility of using MCr as an advanced crystallization technology.

Studies carried out by Macedonio et al. [49–52] show that the introduction of MCr units into the nanofiltration (NF) and RO retentate streams of an integrated membrane-based desalination system that comprises MF/NF/RO processes increases the plant recovery factor to 92.8%, which is higher than that of a RO unit (about 45%) and much higher than that of a typical MSF (10%–20%) [16]. Moreover, it has been experimentally shown that the presence of organic compounds (i.e., humic acid) in the retentate inhibits the growth rate of crystals [53]. This makes it necessary to optimize the NF/RO pre-treatment steps—not only to reduce NF/RO membrane fouling, but also to control the crystallization kinetics, which are linked to the nature and amount of foreign species existing in the highly concentrated brines that emerge from the NF and RO stages. In some studies on MCr [53], a rapid decrease in trans-membrane flux has been observed as a result of crystal deposition on the membrane, reducing the membrane permeability. This problem can be minimized by an appropriate design of the process and by careful control of the operating conditions.

3.4. Case study: A membrane-based system for water and mineral extraction from the sea

As described earlier, seawater contains all the elements in the periodic table from hydrogen to uranium. This section analyzes the potential for economic extraction of NaCl, epsomite ($MgSO_4{\cdot}7H_2O$), and lithium chloride (LiCl), as well as the cost of potable water production from seawater. For these calculations, a typical, large SWRO plant was considered (Table 3).

In the analyzed SWRO plant, seawater arriving at the plant passes through a pre-treatment process (a type of multimedia filter tank) in order to eliminate algae, organic materials, and other particles. Next, before it enters the RO filters to separate the salts, the water passes through a second stage of pre-treatment (MF) to remove smaller impurities. In the subsequent RO process, dissolved salts and other minerals are separated from the water, making it fit for consumption. The resulting brine from the RO contains roughly twice as much salt as seawater. Instead of discharging it into the ocean, brine from the plant is further concentrated via MCr in order to produce more desalted water and salts (Fig. 3). As done in Ref. [53], the RO brine is chemically treated with sodium carbonate (Na_2CO_3) before it enters the MCr step, in order to precipitate 98% of the Ca^{2+} as calcium carbonate ($CaCO_3$). This precipitation/sedimentation step prevents $CaSO_4$ precipitation (which can cause scaling and limit the recovery of magnesium sulfate).

The simulation was performed with the following conditions: ① a MCr recovery factor of 98%; ② solubilities for NaCl and $MgSO_4{\cdot}7H_2O$ of 36.15 g NaCl/100g H_2O and 710 $g{\cdot}L^{-1}$, respectively; and ③ the recovery of all lithium (Li) ions as LiCl. Moreover, it was assumed that the feed-water contained approximately 34 500 $mg{\cdot}L^{-1}$ of total dissolved solids (TDS), 19 000 $mg{\cdot}L^{-1}$ of Cl^-, 10 500 $mg{\cdot}L^{-1}$ of Na^+, 2 700 $mg{\cdot}L^{-1}$ of sulfate ions (SO_4^{2-}), 1 350 $mg{\cdot}L^{-1}$ of Mg^+, 400 $mg{\cdot}L^{-1}$ of Ca^{2+}, 380 $mg{\cdot}L^{-1}$ of K^+, 70 $mg{\cdot}L^{-1}$ of Br^-, and 0.17 $mg{\cdot}L^{-1}$ of Li^+. The feed-water temperature was 20 °C.

Table 3
Characteristics of the studied SWRO desalination plant.

Characteristics	Parameter
Feed (seawater) flowrate ($m^3{\cdot}d^{-1}$)	4.32×10^5
Feed-water TDS ($mg{\cdot}L^{-1}$)	34 500
RO recovery (%)	50
RO operating pressure (MPa)	5.5
RO membrane module	DOW FILMTEC™ SW30HRLE-400
RO salt rejection (%)	99.6
Pre-treatment	Filters and MF

Table 4 summarizes the results of the analysis for the proposed flowsheet in terms of product characteristics, energy consumption, and quantity of produced salts. Table 5 reports the unit cost of the produced desalted water and the revenue for the sale of the salts.

The cost of the desalted water ranges from 0.66 $\$\cdot m^{-3}$ to 0.85 $\$\cdot m^{-3}$ of obtained desalted water. The lowest cost is for a situation in which the water stream is already available at the temperature needed for carrying out the MCr operation, or for a situation in which thermal energy is available at the plant. The estimated water cost takes into account the revenue for the sale of the salts (expressed in Table 5 as $\$\cdot m^{-3}$ of treated seawater). It is clear that the water cost of the integrated RO + MCr system is competitive with the cost of water production using a conventional SWRO desalination process. This is due to the large quantity of recoverable desalted water (93.6%) and to the potentially high quality of the recoverable salts. Moreover, this system minimizes the environmental problems related to brine disposal.

The use of NF, after MF and before RO, offers the possibility of further improving RO performance. An eventual NF pre-treatment will affect the desalination process itself. The turbidity, microorganisms, hardness, most of the multivalent ions, and 10%–50% of the monovalent species (depending on the NF membrane type) are retained through the NF operation. As a result, the osmotic pressure of the RO feed stream is decreased, allowing the unit to operate at higher recovery factors [54]. In fact, according to Refs. [50,55], a coupled NF + RO seawater desalination system can be operated at recovery factors that are 10%–12% higher than those of an SWRO plant using conventional pre-treatment. Taking into account that ① NF membrane cost is almost equal to RO membrane cost, ② NF works at a lower pressure than RO, and ③ NF causes the global recovery factor to increase, the final water cost is positively affected by the use of NF, and is further reduced.

Table 4
Product characteristics for the analyzed flowsheets.

Product characteristics	Value
Plant recovery factor (%)	93.6
Fresh water concentration ($g\cdot L^{-1}$)	0.07
Brine concentration ($g\cdot L^{-1}$)	968
Electrical energy consumption before introducing MCr ($kWh\cdot m^{-3}$)	3.5
Total energy consumption ($kWh\cdot m^{-3}$)	27.3
$CaCO_3$ flowrate ($kg\cdot m^{-3}$ seawater)	0.9224
NaCl ($kg\cdot m^{-3}$ seawater)	22.9
$MgSO_4\cdot 7H_2O$ ($kg\cdot m^{-3}$ seawater)	1.31
LiCl ($kg\cdot m^{-3}$ seawater)	0.00098

Table 5
Summary of cost data.

Items	Value
Total water cost (with revenue from byproduct sale) [a]	0.66–0.85 $\$\cdot m^{-3}$ (the lowest value is for available waste heat)
Revenue from $CaCO_3$ sale	0.057 $\$\cdot m^{-3}$ seawater
Revenue from NaCl sale	0.687 $\$\cdot m^{-3}$ seawater
Revenue from $MgSO_4\cdot 7H_2O$ sale	0.745 $\$\cdot m^{-3}$ seawater
Revenue from LiCl sale	0.020 $\$\cdot m^{-3}$ seawater

[a] The membrane life is considered equal to 10 years for MF and RO and to 5 years for MCr. Plant life = 30 years; electric cost = 0.11 $\$\cdot kWh^{-1}$; and heating steam cost = 0.0032 $\$\cdot lb^{-1}$ (1 lb = 0.453592 kg). The selling price is 30 $\$\cdot t^{-1}$ for NaCl; 570 $\$\cdot t^{-1}$ for $MgSO_4\cdot 7H_2O$; 62 $\$\cdot t^{-1}$ for $CaCO_3$; and 2 $\$\cdot kg^{-1}$ for LiCl.

3.5. Membrane-based vapor water capture

In addition to desalination and wastewater treatment, water capture from industrial waste gaseous streams can become a source of water supply. In fact, water consumption by industries represents around 22% of global water consumption [56]. At present, no commercial technology is available for evaporated wastewater recovery from industrial processes [57]. Cooling with condensation [58], liquid and solid sorption [59], and dense membranes [60,61] are the technologies that are traditionally utilized for water recovery from evaporated waste gaseous streams. Their disadvantage is that dense membranes operate under high pressure, since a pressure difference is necessary to promote the permeation of the water vapor through the membrane. This, in turn, results in compression, high energy consumption, and high costs [57]. Porous hydrophilic polymer membranes [62] were utilized as a dehumidification system. Drioli and coworkers [57,63–66] recently introduced the membrane condenser as an innovative membrane unit operation for water recovery from waste gaseous streams (Fig. 4).

The working principle of a membrane condenser is as follows: The humid gaseous stream is brought into contact with a microporous hydrophobic membrane. The hydrophobic nature of the membrane inhibits the liquid from penetrating into the membrane pores. The liquid water is therefore retained on the retentate side of the membrane. If the temperature in the membrane condenser module is lower than that of the waste gaseous stream, it reaches a supersaturation state, allowing more water to be recovered. Compared with dense membrane-based technology, the membrane condenser does not require high pressures. Moreover, it has been proved [63] that the membrane condenser offers the opportunity to control the quality of the produced liquid water.

4. Conclusions and future perspectives

In recent years, the success of RO technology has come to symbolize the growth of membrane-based technology. The success of RO treatment is due to improvements in membrane performance, such as better membranes and materials, increased salt rejection and flux, improved membrane life and process designs; to this process having the lowest energy consumption with respect to thermal processes; to improvements in pre-treatment processes; and to increases in plant capacity. Today, membrane-based technologies are increasingly considered as pre-treatment for RO plants; they provide superior quality performance by enabling higher permeate

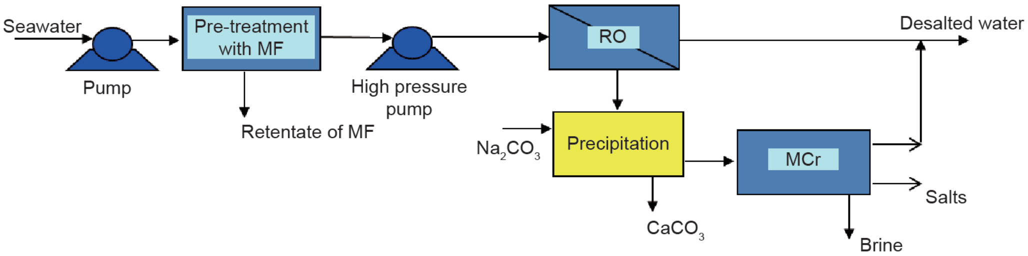

Fig. 3. Flowsheet of the analyzed SWRO desalination system.

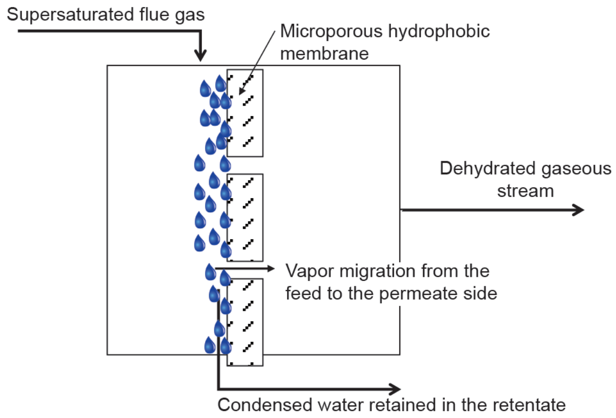

Fig. 4. Scheme of the membrane condenser process for the recovery of evaporated "waste" water from a gaseous stream. (Reprinted with permission from Ref. [57]. Copyright 2013, American Chemical Society)

flux, a greater recovery factor, and a longer membrane lifetime. However, the problem of membrane fouling and biofouling appears to be the most critical issue for these technologies, and brine disposal is another significant issue. Cost-effective and environmentally sensitive concentrate management is now recognized as a significant challenge toward the extensive implementation of desalination technologies. The third problem affecting these technologies is related to the energy consumption of the process. International projects focusing on minimizing these problems have been funded in past years, such as the European research project MEDINA [67], the Mega-ton Water System project in Japan [68], and the SEAHERO R&D project in Korea [69,70]. In the first part of these projects, the emphasis has mainly been on increasing the desalination capacity. However, in the second part of these projects, brine-disposal issues have also been addressed. Hybrid systems with MD and PRO units have been proposed for the extraction of valuable resources from brine, the minimization of the environmental impact of brine, and the recovery of energy. Therefore, IMSs offer the possibility of a new era in desalination processes: the third generation of desalination installations. IMSs can be essential tools for achieving the objectives of ZLD, total raw materials utilization, and low energy consumption.

Compliance with ethics guidelines

Francesca Macedonio and Enrico Drioli declare that they have no conflict of interest or financial conflicts to disclose.

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