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Membrane crystallization for salts recovery from brine—an experimental and theoretical analysis

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ABSTRACT

Integration of innovative membrane processes such as membrane distillation (MD) and membrane crystallization (MCr) with conventional pressure-driven operations provide interesting gateways to recover water and minerals from brine at cost competitive with traditional techniques and with improved quality of the salts extracted. Membrane development is one of the most important factors for future progress and commercialization of MD and MCr, thus, in this study, the performance of different poly(vinylidene fluoride) membranes have been tested for water production from (1) NaCl solutions, (2) synthetic sea water, and (3) brine. The utilized membranes have also proved their stability in treatment of saturated solutions for the recovery of high-quality epsomite crystals. In desalination, MD and MCr provide, besides water recovery factors above 90%, the possibility to recover minerals from brine that can partly contribute to the existing mineral extraction industry. This study aims also to give an outlook of the ambitious step toward zero liquid discharge in desalination, where components such as magnesium, barium, and lithium might be recovered from brine in high quantities and qualities. The positive prospects of intelligent integrations (reverse osmosis [RO] + MD + MCr) for water production and mineral recovery are also shown by estimations of process intensification metrics, such as mass and waste intensities. The improvement of the process with continued treatment of RO brine by means of MD and MCr is illustrated by the significant decrease of these parameters.

Keywords: Membrane crystallization; Mineral recovery; Water production; PVDF membranes

1. Introduction

Progress in membrane engineering has been realized through development of large-scale membrane-based desalination plants in countries with freshwater limitations. The transformation from conventional distillation techniques to membrane-based desalination is justified due to the close association of membrane engineering with the process intensification strategy (PIS) [1]. PIS introduces goals and guidelines for

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improved sustainable production including minimization of input (raw materials, energy, equipment, etc.) while maximizing the output (product quality, product quantity, energy recovery, reuse, etc.) together with waste reduction and elimination of other negative impacts on human and environment.

In desalination, reverse osmosis (RO) is the major used technology [2]. The motivation for using RO compared to conventional thermal technologies is the reduced energy requirements because no phase change, compactness etc. occurs. However, there is still need for improvements in terms of water recovery factors, problems in brine disposal, and electrical energy requirements. Therefore, membrane distillation (MD) and membrane crystallization (MCr) are being explored, as novel membrane operations, for improving desalination. Membrane contactor technologies such as MD and MCr are getting more attention due to the minimal impact of concentration on process performance and reduced fouling. MD and MCr work on the principle of vapor–liquid equilibrium where the membrane does not act as a separation unit but solely as a contactor between two interfaces. The driving force in MD and MCr is the temperature gradient across the membrane operated, in general, at feed temperatures in the range of 40–80˚C which makes the process able to run with waste heat or renewable energy sources. MD and MCr can be stand-alone processes as seen with the first commercialized MD plant from Aquaver and in Saudi Arabia where a small MD plant has been constructed based on Memsys technology [3–5]. MD and MCr can also be integrated with RO to elevate the overall recovery factor above 90%. This might realize the aspiring objective of zero liquid discharge (ZLD) in desalination. The aim of ZLD is to reduce brine disposal problem and enhance water production by only producing two streams: water and minerals (Fig. 1).

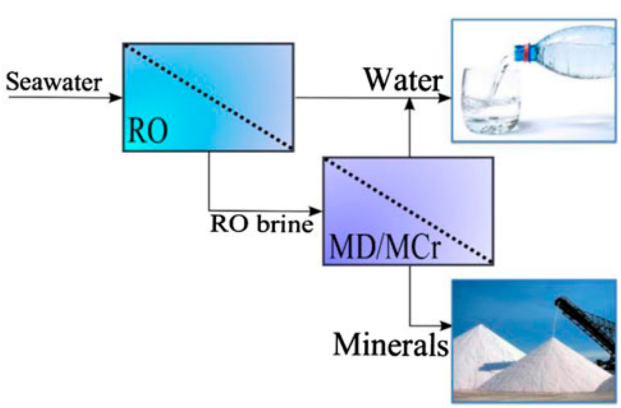

Fig. 1. Flow sheet for integrated systems for approaching ZLD in desalination.

Therefore, another advantage of mineral production from RO brines is the possibility to produce a large amount of minerals that can be used, for example, in the emerging non-fuel technologies. The mining industry, which normally produces the required minerals, is facing problems of mineral depletion, water shortages, and high energy requirements. In fact, mineral production from mining industry requires large amounts of energy and water. In particular, the outlook of water shortage in future has made water in mining a hot topic and has constrained the mining industry to look toward alternative water resources and water production methods to meet their increasing demands. A solution could be to look toward the sea. In fact, sea contains almost all the components in the periodic table. However, the very low concentration of valuable components in sea water and the high expenses associated with the extraction methods have suppressed mineral production from sea water. Nevertheless, the growth in desalination capacities and the proposed strategy of integrated membrane operations have resulted in an opportunity for increasing the concentration of valuable components in the brine stream and simultaneously produce freshwater by means of MD and MCr. Further advantages of using MCr for concentration and recovery of components from brine lies in the fact that this novel process, at low energy requirements, is able to produce crystals of high quality in terms of purity, controllable crystal size, narrow crystal size distribution, and adjustable polymorph selection, etc. [6]. In literature, various scientific publications [1,6–16] can be found proving the advantages of MCr with respect to conventional crystallization processes, in particular in terms of "facilitated" and "controlled" crystallization process. In fact, the basic peculiarity of MCr is the possibility to perform well-behaved crystallization processes. In this process, the solvent evaporation through the membrane allow to modulate the final degree and the rate for the generation of the supersaturation, to control the final properties of the crystals produced both in terms of structure (polymorphism) and morphology (habit, shape, size, and size distribution), for both small and large molecules.

Unlike the positive aspects of MD and MCr, these processes suffer from some limitations and one of the biggest challenges to overcome in order to arrive to commercialization of MD and MCr is membrane development. Therefore, many research activities focus on preparing membranes specifically developed for MD. Membrane material and specific membrane features are important for MD and MCr performance. Membrane hydrophobicity is vital for MD and MCr processes and in particular materials, such as poly (vinylidene fluoride) (PVDF), polypropylene (PP), and polytetrafluoroethylene (PTFE), are used in MD. In general fluoropolymers have low surface tension, high thermal stability, and improved chemical resistance which make them excellent materials for membrane operations [17]. The hydrophobicity of PVDF is not as high as PP or PTFE, but PVDF has the advantage that it can be easily dissolved in common solvents [18] and studies are in progress related to the possibility to prepare PVDF membranes utilizing green solvents [19].

In this paper, MD and MCr have been utilized with PVDF lab-prepared membranes for the treatment of saturated brines. In particular, the first part aims to experimentally evaluate different membranes (1) for the treatment of synthetic sea water and RO brine by means of direct contact membrane distillation (DCMD) and (2) for the recovery of targeted compounds (here magnesium sulfate) from saline solutions by means of MCr. The second part of the paper describes, theoretically, the prospects of utilizing MD/MCr for concentration and recovery of valuable components from RO brine of a membrane-based desalination system. In the last part of the paper, some process intensification metrics have been evaluated for membrane desalination processes with MCr units.

2. Materials and methods

2.1. Experimental evaluation of different PVDF membranes

The lab-prepared PVDF hollow-fiber membranes were spun by the dry/wet technique described elsewhere [20,21] and their main characteristics are reported in Table 1. The membranes have been tested in MD and MCr applications of (1) NaCl solutions, (2) sea water, (3) RO brine concentrations (Table 2), and (4) with saturated $MgSO_4$ solutions. Sea water and brine compositions have been estimated on the following assumptions: (1) sea water intake has a salinity at 4.0%; (2) RO recovery factor is 51%; (3) salt rejection of RO membrane is 99.7%; and (4) RO brine, before being further concentrated through MD and MCr, is pretreated with the addition of Na_2CO_3 for removal of 98% of calcium to prevent gypsum scaling on MD/MCr membrane surface.

Table 1
Properties of the tested PVDF membranes for MD and MCr application

Fiber	M1	M2
Outer diameter O.D. (mm)	1.75	1.78
Inner diameter I.D. (mm)	0.94	1.40
Thickness δ (mm)	0.40	0.19
Young's modulus Emod (N/mm^2)	65.76	150.53
Tensile stress at break Rm (N/mm^2)	3.86	4.49
Elongation at break ε break (%)	259.95	223.30
Avg. pore size (μm)	0.47	0.52
Porosity (%)	80.77	65.44

MD and MCr have been carried out on a small lab-scale plant built to fit the membrane modules. The plant is shown in Fig. 2 and consists of a 500 ml feed tank submerged in a heating bath to maintain the required temperature. The flux is obtained by measuring the increment in volume using a 250 ml graduated cylinder immersed in a cooling bath. The flow rate is obtained by two peristaltic pumps and inlet temperatures are measured with thermocouples on retentate and permeate side, respectively.

The membranes have been tested having feed solution in shell side and permeate in the lumen side of the membrane. This configuration was chosen in order to avoid eventual fiber blocking during the crystallization process. The DCMD experiments were performed with retentate and permeate flow rates constant and equal to 100 and 20 ml/min, respectively. Retentate and permeate temperatures at the inlet of the membrane module were kept at 36.1 ± 1.4 and 24.7 ± 2.0˚C, respectively.

2.2. Prospect of recovery of valuable components from RO brine

The theoretical evaluation of the minerals that can be potentially recovered from RO brine has been carried out considering (1) the total current desalination capacity (i.e. 66.4 million m^3/d [2], 60% of which is produced by RO), (2) a sea water salinity of 3.5%, (3) RO with a recovery factor of 51% and a salt rejection of RO membrane of 99.7%, and (4) the total current desalination capacity is produced through RO with the characteristics reported in (3). Furthermore, it is considered that the RO brine is chemically treated with Na_2CO_3 to remove calcium ions for preventing gypsum scaling on the membrane surface [9]. In general, scaling on membrane surface in MD and MCr can be avoided by adjusting feed flow rates, temperatures, and membrane configuration. However, components such as calcium carbonates, calcium sulfates, and silica might reduce membrane performance by difficult manageable scaling phenomena [22,23].

The estimated amount of some recoverable components from RO brine have been compared to the

Table 2
Composition of synthetic sea water and brine

Composition	Synthetic sea water (ppm)	Synthetic brine (ppm)
Na^+	12,500	26,478
Mg^{2+}	1,520	3,101
Ca^{2+}	490	20
Cl^-	22,300	45,500
SO_4^-	3,189	6,507
HCO_3^-	150	107

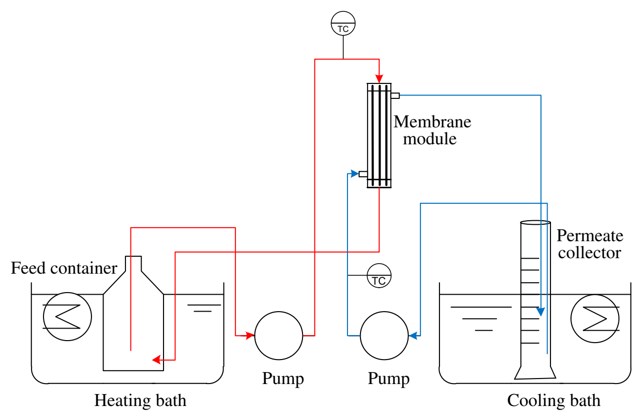

Fig. 2. Schematic representation of the lab-scale MD plant used for MD and MCr tests.

annual production of each component (Eq. (1)) based on US Geological Survey data (mineral commodity summaries) [24] in order to estimate the potential degree of replacement:

$$\text{Degree of replacement (\%)} = \frac{\text{Potential recovery from RO brine (If ZLD is obtained)}}{\text{Annualexisting recovery}} \cdot 100 \quad (1)$$

2.3. Estimation of process intensification metrics

With the aspiration of renewing existing methodologies or developing new technologies in the logic of PIS, the following indicators have to be taken into account: environmental, economic, and social indicators. These metrics (Table 3) have been developed (1) to clearly assess how the particular process is responding to sustainability and (2) they can be used to define targets and standards for benchmarking, and (3) to monitor progress [25].

The integration of different membrane technologies (such as RO + MD + MCr) can have positive impacts on various industrial productions. An example is shown in the present paper, where metrics have been estimated for a lab-scale MD and MCr plant.

3. Results and discussion

3.1. Experimental evaluation of different PVDF membranes

As previously described, lab-prepared PVDF hollow-fiber membranes have been tested. Transmembrane flux and temperature difference between retentate and permeate side have been measured and the obtained results are reported in Fig. 3. Membrane M2 provides an evidently higher flux compared to membrane M1 (Fig. 3(a)), although the driving force for M1 is higher (Fig. 3(b)).

The better performance in DCMD of M2 is accounted to the lower thickness of the membrane. Low membrane thickness implies reduced mass transfer resistance. Knudsen diffusion, molecular diffusion, and/or viscous flow are the resistances influencing mass transfer through the membrane in DCMD [26]. However, a conflict exists between the requirements of high mass transfer associated with thinner membranes and low conductive heat losses achievable using thicker membranes. In fact, thermal efficiency in DCMD increases gradually with the growing of membrane thickness and an optimization between the two requirements has to be found. Moreover, it can be observed that the two tested solutions (1) NaCl 28.02 g/l and sea water and (2) NaCl 57.18 g/l and RO brine give origin to almost the same flux (Fig. 3(a)). In general, the vapor pressure is affected by increase in concentration and therefore a higher concentrated solution is expected to provide a lower flux. According to the performance of the membranes utilized in this study, they are not reacting negatively to the higher concentrations and the membranes are able to maintain the same performance throughout the experimental time. Moreover, the same membranes have been utilized in all the carried out tests (NaCl, Sea water, and brine), only with a slight cleaning with distillate water after finishing each test and subsequent drying with air to restore hydrophobicity, thus the membranes are also resistant toward continued treatment cycles.

The conductivity of permeate has been measured at the end of each test to classify the probability of pore wetting. For the conducted DCMD tests, the constant trend of transmembrane flux together with the low permeate conductivity (Fig. 4) proves that no wetting occurred, at least during the operative time.

Table 3
Metrics for evaluation of the performance of the entire process

Metric	Definition
Mass intensity (MI)	$\frac{\text{Total mass}}{\text{Mass of product}}$
Waste intensity (WI)	$\frac{\text{Total waste}}{\text{Mass of product}}$
Productivity/size ratio (PS)	$\frac{\text{Productivity}}{\text{Size (membranes)}}$
Productivity/weight ratio (PW)	$\frac{\text{Productivity}}{\text{Weight (membranes)}}$
Flexibility	Number of processes that the unit is able to handle
Modularity	Influence of plant size on productivity

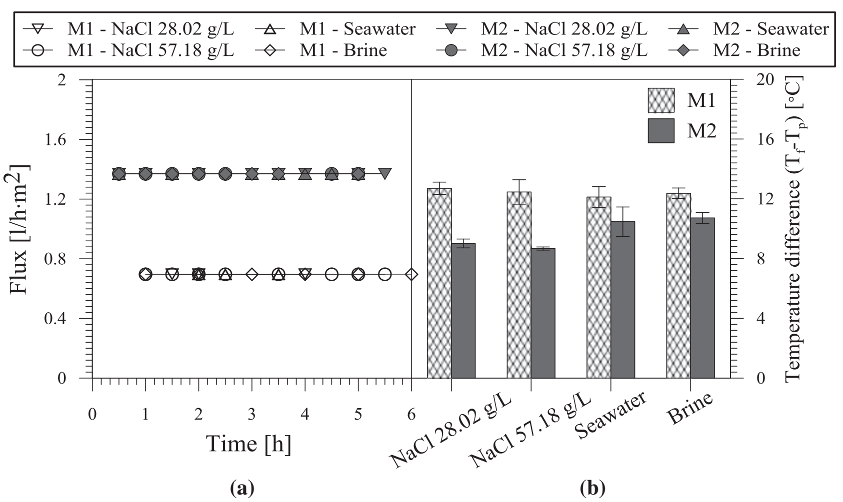

Fig. 3. (a) Transmembrane flux and (b) temperature difference for DCMD treatment of NaCl solutions, synthetic sea water and RO brine.

An eventual wettability of the membranes will affect not only the permeate quality negatively, but also will depress the membrane performance in terms of flux. Therefore, the higher transmembrane flux for membrane M2 was only due to the superior membrane structure.

3.2. MCr of epsomite

Membranes M1 and M2 have been tested in MCr of $MgSO_4 \cdot 7H_2O$ (epsomite). M1 has also been tested with different flow rates (100 and 140 ml/min). The obtained transmembrane flux and temperature difference are shown in Fig. 5. The performance of M2 is again better than that of M1. The utilized plant did not allow detecting of alteration in performance between the two utilized flow rates. It is expected, in fact, to obtain a higher flux with a higher flow rate

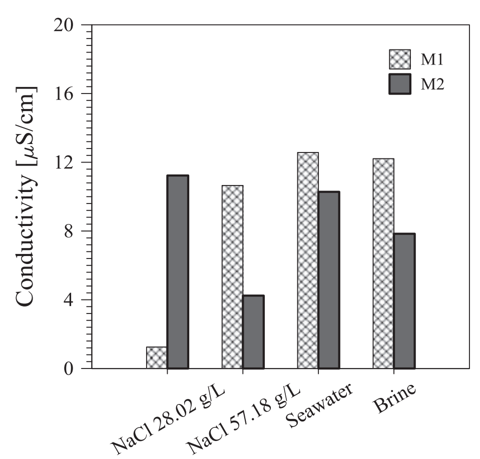

Fig. 4. Conductivity of permeate for the carried out DCMD tests with NaCl solutions, sea water, and RO brine used as feed.

due to decrease in boundary layer resistance and thereby temperature polarization [27].

Despite the utilized plant not allowing appreciating a difference in membrane performance in terms of transmembrane flux between the two tested feed flow rates, the latter is an important parameter which might cause a change in crystal quality. Optical microscope images (Fig. 6) have been utilized to characterize the obtained crystals in terms of mean diameter (d_{m}), coefficient of variation (CV), and growth rate (G). CV has been estimated by Eq. (2), whereas growth rates and nucleation rates have been estimated on the basis of the Randolph-Larson model (Eqs. (3) and (4)):

$$\mathrm{CV} = \frac{F_{80\%} - F_{20\%}}{2 \cdot F_{50\%}} \cdot 100 \quad (2)$$

$$\ln(n) = \frac{-L}{Gt} + \ln(n^0) \quad (3)$$

$$B^0 = n^0 G \quad (4)$$

where F is the cumulative percent function given by the crystal length at the indicated percentage. n is the population density, L is crystal size, G is growth rate, t is retention time, and n^0 is population density at $L = 0$.

The time of crystals recovery is reported in Table 4: in each test, two crystal samples have been extracted from the feed tank and analyzed. It has been observed that, as expected, nucleation occurs earlier at the highest flow rate compared to the lower flow rate. This suggested that effectively transmembrane flux was higher in the test carried out utilizing the highest feed flow rate thus allowing faster supersaturation achievement. The discrepancy with what was observed in Fig. 5 was due to the fact that the cylinder utilized to measure the increase of permeate volume had a graduation too wide to allow appreciating difference in permeate fluxes in the two performed tests. Moreover, in the test carried out at the highest flow rate, the mean diameter and crystal growth rate are larger compared to those achieved in the test performed at the lowest flow rate (i.e. 100 ml/min). Finally, the low values of CVs (Table 4) obtained in the present study

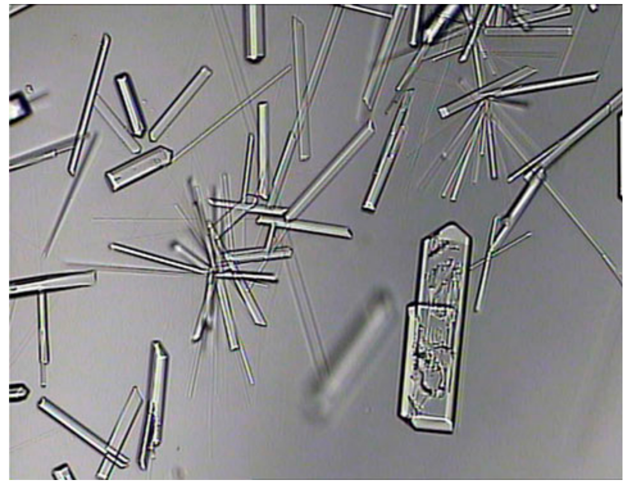

Fig. 6. Epsomite crystals produced by means of MCr.

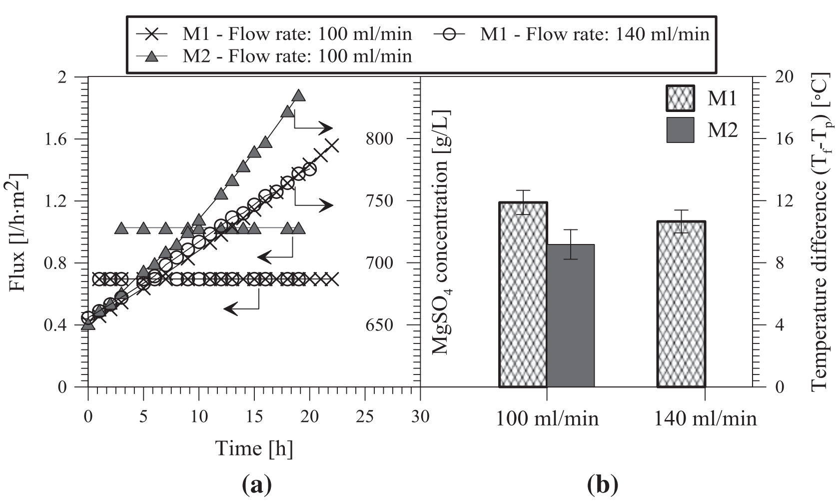

Fig. 5. (a) Transmembrane flux and $MgSO_4$ concentration (b) temperature difference for MCr treatment of $MgSO_4$ solution (initial concentration = 651 g/l).

Table 4
Crystal characteristics obtained with membrane M1 at different flow rates

	Time of recovery (h) Sample		Mean diameter (μm) Sample		CV (%) Sample		Growth rate (μm/min) Sample	
Membrane type	1	2	1	2	1	2	1	2
M1 100 ml/min	21	22	367.2	361.5	33.58	41.44	0.1111	0.09752
M1 140 ml/min	19	20	589.2	598.4	40.95	30.52	0.3576	0.4478

with respect to those achieved utilizing conventional crystallizer (~50%) validate the superior crystal product obtainable through MCr technology.

3.3. Prospect of recovery of valuable components from RO brine

The progress in MD and MCr in the last decade and the continued increase in numbers of different compounds recovered by means of MCr (i.e. $MgSO_4$ in this study; NaCl in [9–11]; Na_2SO_4 in [12,28]; and various biomolecules in [8,13,14]) indicate promising prospects for future applications, including the possibility to reach the goal of ZLD in sea water desalination. Different methodologies have been suggested and applied for obtaining near to ZLD, including integration of RO and reverse electrodialysis [29], RO + forward osmosis and salt recovery [30], NF–RO [31], UF–NF–RO–MSF-Crystallization [32], RO + wind-aided intensified evaporation and MCr [15], and NF-RO-MCr [16].

Some ions that can be recovered from RO brine are barium and strontium in the form of barite and celestite, respectively, at around a recovery factor of 54 and 64%, respectively. For what concerns the barium components, these can be of great interest to recover due to the huge amount utilized in the oil and gas industry as weighing material in drilling mud [33], proved also by the significant price increase observed over the last years (i.e. from 77 $/ton in 2010 to 115 $/ton in 2013 [34]). The other component which can be recovered from RO brine at initial treatment with MD and MCr might be celestite, which might substitute a part of the barite used for drilling mud. Strontium recovery from RO brine might partly replace mining by a contribution of 90% (Fig. 7). According to USGS, the average price of strontium import for USA in 2013 was 50 $/ton [35]. Thanks to the higher concentration of strontium in RO brine (Table 5), the recovery of strontium compounds by means of MCr might add a higher economic benefit as compared to barium recovery.

Nevertheless, the recovery of strontium and barium compounds from RO brine can also create scaling problems and they can be incorporated into other crystals lattices during the crystallization process [11]. In particular, if strontium and barium are not recovered separately before NaCl crystallization, their incorporation into NaCl crystals are highly probable due to the much higher amount of NaCl compared to barium and strontium [11]. Therefore, evaluation of barium and strontium precipitation in MCr is of great interest for enhancing the well-controlled crystallization process provided by MCr.

Despite the low price of NaCl recovered from brine (8.5 $/ton [34]), a significant economic benefit can be achieved if some or all the NaCl is being recovered from desalination plants. In fact, previous studies have shown that, for a system consisting of RO and MCr operating at overall recovery factors around 70% and capacity of 739.6 m^3/h [16], almost three million dollars is the yearly profit for selling the salts

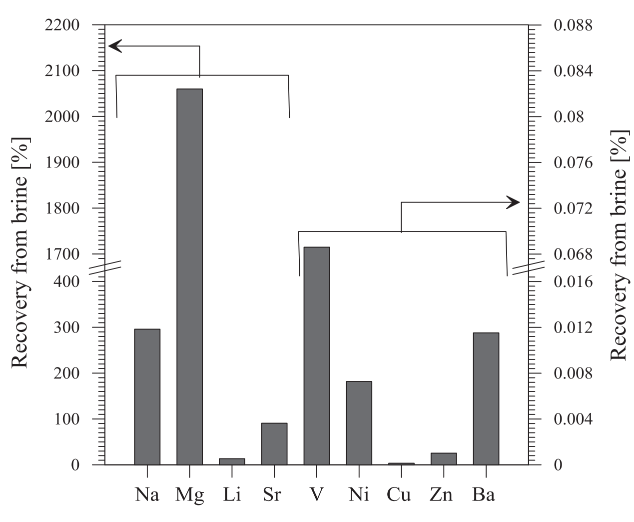

Fig. 7. Potential recovery of different metals from brine with respect to the annual mining. The annual mining is based on US Geological Survey [34]. The amount of Mg and Li mined in US is not available.

Table 5
Composition of sea water, RO brine, and RO brine after chemical treatment with Na_2CO_3 for some chosen ions of interest

	Sea water (ppm)	RO brine (ppm)	RO brine after addition of Na_2CO_3 (ppm)
Sodium Na	10,800	22,036	22,800
Chloride Cl	19,400	39,583	39,583
Magnesium Mg	1,290	2,632	2,632
Sulfate SO_4^-	2,790	5,693	5,693
Potassium K	392	800	800
Calcium Ca	411	839	16.8
Lithium Li	0.17	0.35	0.35
Hydrogen carbonate HCO_3^-	131	268	89.4
Phosphor P	0.088	0.18	0.18
Vanadium V	0.0019	0.0039	0.0039
Chromium Cr	0.0002	0.0004	0.0004
Manganese Mn	0.0004	0.0008	0.0008
Nickel Ni	0.0066	0.013	0.013
Copper Cu	0.0009	0.002	0.002
Zinc Zn	0.005	0.01	0.01
Selenium Se	0.0009	0.002	0.002
Rubidium Rb	0.12	0.24	0.24
Strontium Sr	8.1	17	17
Cesium Cs	0.0003	0.0006	0.0006
Barium Ba	0.021	0.043	0.043
Uranium U	0.0033	0.0067	0.0067

produced by MCr (Estimated NaCl selling price = 30 $/ton) [16]. The great profits of selling the salts will cause a strong reduction in water price and will make the salt production the primary requisite.

As obtained experimentally in this study, it is possible to obtain high-quality $MgSO_4$ crystals and in Fig. 7, it is illustrated that the potential magnesium recovery from brine is far more of what is needed and extracted today. However, due to the fact that the production of magnesium in US is not available from US Geological Survey, the magnesium degree of replacement is lower than that reported. Magnesium is one of the components which is already extracted from sea water as magnesium oxide. It is also extracted from mining as magnesite.

Another interesting component to recover from RO brine is lithium. Today it is mainly recovered from minerals in the mining industry or from high content salt lake brines. Extraction of lithium directly from sea water suffers from relatively high production costs and low extraction amounts. The lithium production costs from sea water is estimated to be 80 $/kg, which is not competitive with respect to the recovery cost from mining of spodume (6–8 $/kg) or from salt lake brines (2–3 $/kg) [35]. If MCr process is able to achieve enough high recovery factors (above 99%), the process might be able to replace 13% of the lithium amount, which is today extracted from mines (Fig. 7).

Other interesting components to be recovered from RO brine might be copper. US Geological Survey has estimated a total world copper production in 2013 to be 17,900,000 tons, with Chile as the dominant producer [34]. Considering that, today, the accessible copper reserves account for 690,000 thousand metric tons [34], if the mining extraction of copper continues at the current level, it is close to mineral depletion. Besides the mineral depletion, also the severe environmental impacts caused by the mining industry have to be considered. An example can be found in the study by Northey et al. [36], where energy, greenhouse gas, and water intensity, based on available company data, were analyzed. It was found that on average 22.2 GJ/t Cu (energy intensity), 2.6 t CO_2-e/t Cu (greenhouse gas intensity), and 74 kl/t Cu (water intensity) have been used in copper production. In general, the energy requirements and greenhouse gas emission depend on ore grade and fuel sources. Water is used for moisture control, dust suppression, cooling, and in grinding and, consequently, natural water resources are being depleted simultaneously [36]. Therefore, desalination is implemented also to supply the mining industry with freshwater resources. On the other hand, MCr does not consume but produces water, and the energy consumption cannot be so high. In fact, it has been estimated that an integrated MCr plant, similar to the one in Fig. 1 with an additional pretreatment

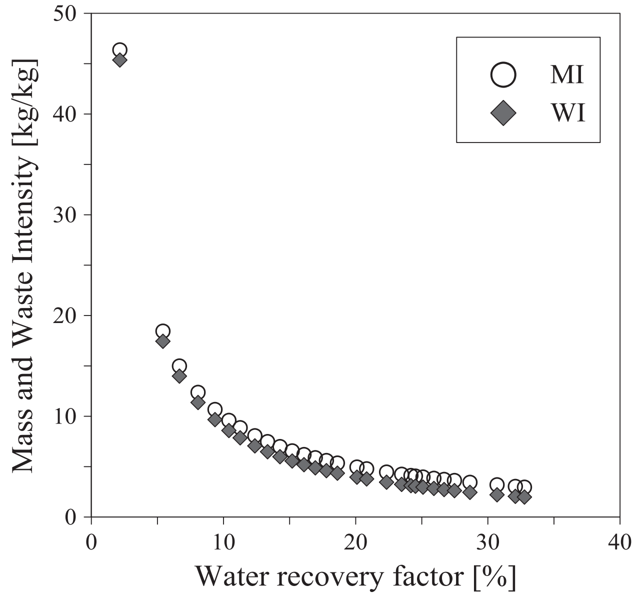

Fig. 8. Mass and waste intensity for a lab-scale MD and MCr plant. The water recovery factor is with respect to the concentration of RO brine.

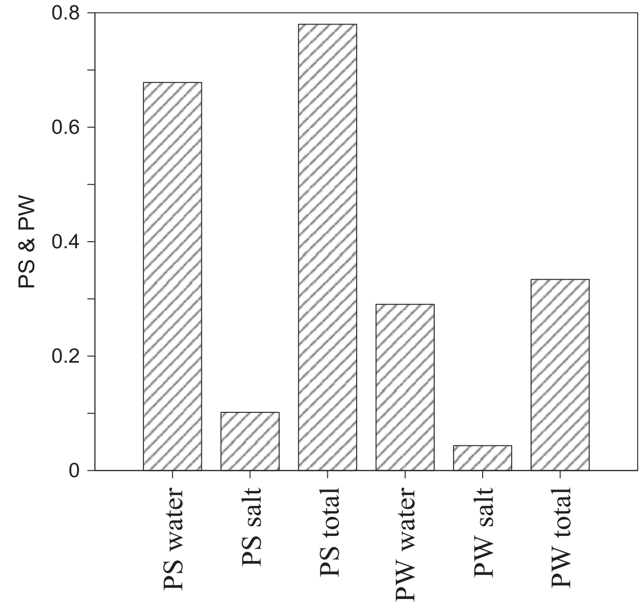

Fig. 9. Productivity with respect to membrane size and weight illustrated with the difference in only water and salt production and the combined productivity.

step consisting of micro- and nanofiltration, consumes 18.3 kWh/m^3 of freshwater produced [16]. However, due to the relatively low temperature utilized in MCr, waste heat or energy recovery systems can be used, thus reducing the energy requirements to below 2.59 kWh/m^3 [16].

3.4. Estimation of process intensification metrics

The process intensification metrics estimated in this work are mass intensity, waste intensity, productivity/size ratio, and productivity/weight ratio (Table 3). Metrics have been calculated for a MD/MCr plant utilizing PP membranes with surface equal to 0.2 m^2 and weight equal to 0.467 kg. In the estimations of new metrics, the solution to be treated has been considered as synthetic RO brine (Table 2) with feed inlet temperatures of 38.4 ± 1°C. These operative conditions give rise to an average flux of 0.678 kg/(m^2 h), salt production of 20.34 g/h, and concentration factor of 4.5. The described values have been obtained experimentally and have been utilized to estimate the same parameters in a larger scale desalination process.

The improvement of the process with continued treatment of RO brine by means of MD and MCr is illustrated by the significant decrease in mass and waste intensities (Fig. 8). The positive trend is also observed when productivity with respect to membrane size and weight is estimated (Fig. 9). The reason

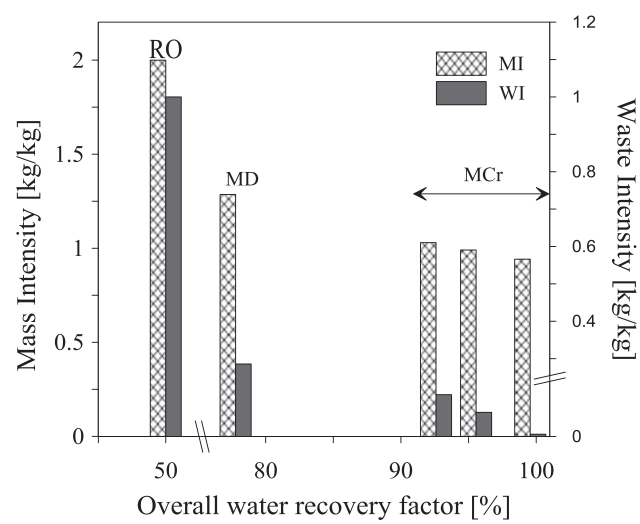

Fig. 10. Decrease in mass and waste intensities for the integrated membrane system consisting of RO, MD, and MCr (Only NaCl production has been taken into account).

for the small contribution of salt production to the overall productivity is that the lab-scale experiment has only been performed until the beginning of NaCl precipitation. However, the continued recovery of NaCl and other salts can further significantly increase the productivity and decrease the mass and waste intensities.

To demonstrate the potential decrease of mass and waste intensities, the treatment of 100 m^3 of RO brine has been considered (Fig. 10) and the calculations have been based on the results obtained from the lab-scale plant. RO is only able to recover around 50% of freshwater, thus relatively high MI and WI are obtained at this stage. The introduction of MD and MCr reduce MI and approaching unity. The objective of ZLD also entails WI to reach zero.

4. Conclusion

High water stress, and increasing energy consumptions and mineral depletion are all already critical issues. Process engineering is one of the disciplines more involved in the technological innovations necessary to face these strongly interconnected problems. As a matter of fact, water is also needed for energy generation (e.g. as cooling component); energy is also needed in desalination and for raw material production (especially in mining where large amount of energy and water are necessary). Membrane technology can represent a problem-solver with intercorrelated solutions. In fact, traditional membrane separation operations (e.g. MF, UF, NF, and RO), widely used in many different applications, can be today combined with new membrane systems (such as MCr) for the design of highly integrated membrane processes that are aimed at higher water production, lower energy consumption, and minerals formation.

In this paper, two different PVDF lab-made membranes have been tested in MCr operation. The results achieved in the crystallization of epsomite proved that the membrane characteristics influence the process performance not only in terms of transmembrane flux, but also in terms of crystal characteristics. Moreover, high-quality crystals can be obtained. Therefore, MCr can be utilized in the future desalination plants for the recovery of other compounds of high economic benefit, such as barium, strontium, lithium, and copper, by utilizing integrated systems RO–MD–MCr. To this aim, a theoretical study has been performed and the obtained results show that strontium and lithium recovery from RO brine might partly replace mining by a contribution of 90 and 13%, respectively. With respect to mining, integrated membrane operations have the additional advantage of not consuming water; with respect to conventional desalination, processes have the benefit of reducing the amount of discharged brines as illustrated by the positive effect on mass and waste intensities.

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