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Experimental and economical evaluation of a membrane crystallizer plant

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ABSTRACT

Nowadays water scarcity is being recognized as a present and future threat to human activities throughout the world. Therefore, a definite trend to develop alternative water resources for a *sustainable development* can be observed. Since much of this precious limited supply is either locked in polar ice or it found in a limited number of lakes and rivers throughout the world, the largest potential source of alternative water is represented by *salt water* (97% of available water) and requires desalination. Today, the most commonly used desalination technology is Reverse Osmosis (RO) due to its low energy consumption and high recovery factor (≈40–50%) with respect to thermal processes (usually characterized by a recovery factor of about 10–20%). This means, less highly-concentrated brine to be discharged which can affect aquifers and marine environment and which can also result in financial penalties if toxicity standards are not met.

In this work, the possibility of using Membrane Crystallizer (MCr) on Nanofiltration (NF) brine streams for the quasi-total recovery of the desalted water combined to solid salts production has been investigated. Special focus has been placed on the stability and control of the process by avoiding crystal deposition inside the membrane module and/or on the membrane surface. The results achieved through the experimental tests showed, apart an initial transitory stage, an almost constant trend of the trans-membrane flux. This encouraging outcome was due to the optimization of the process parameters and to the improvement of an existing MCr lab-plant.

Keywords: Water stress; Desalination; Membrane contactor technology; Economical evaluation

1. Introduction

The world's potable water supply, available to support the human, agricultural, and industrial needs, is being depleted at an alarming rate and the forecasts are for an increased water scarcity in many regions around the globe by the year 2020 due to: (i) the continuous growth in population, tourist infrastructure and industrial development, (ii) the deterioration of water quality as a consequence of indiscriminate discharge of both domestic and industrial effluents without adequate treatments. Water usage is globally increased by six times in the past 100 years and will double again by 2050.

Water scarcity, however, encouraged the development of alternative water resources and, because 97% of available water is represented by salt water, unavoidable was the recourse to sea for alleviating the worldwide shortage in water.

Nowadays, the global installed desalination capacity stands at 52 million m^3/d and it is expected to increase until to 107 million m^3/d in 2016. Among the desalination technologies, membrane-based systems are the most widely used processes, whose installations account for close to 80% of all desalination facilities and provide about 50% of the total capacity of desalination plants [1].

On the other hand, seawater desalination plants cause some local negative impacts on the environment due to the dumping of their concentrate waste

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streams, often into surface waters or into the oceans. It is therefore necessary to develop alternative methods to ensure a more sustainable grow of desalination processes. Membrane Engineering provides a possible solution, through the integration of conventional pressure-driven membrane operations (such as Reverse Osmosis and Nanofiltration) with the recent and advanced Membrane Crystallizer operation. MCr has been recently proposed as an innovative technology for the quasi-total recovery of the desalted water combined to solid salts production.

The defining phenomenon of a MCr is relatively simple. In this operation, a heated, aqueous feed solution is brought into contact with one side (feed side) of a hydrophobic, microporous membrane. The hydrophobic nature of the membrane prevents the penetration of the aqueous solution into the pores, resulting in a vapor–liquid interface at each pore entrance. The driving force of the process is linked to both the partial pressure gradient and the thermal gradient between the two membrane sides. When the feed is water containing salts (as in the case of sea- and brackish-water), the solvent will be vaporized at the liquid/vapor interface and then passes as vapor through the membrane pores. As a consequence, the feed solution will be concentrated above its saturation limit, thus achieving a metastable state in which crystals may nucleate and grow.

MCr has several advantages with respect to the other separation processes, some of which are:

- MCr can be used for the treatment of highly concentrated solutions (i.e. non-volatile solute) without suffering the large drop in permeability observed in other membrane processes such as the pressure-driven membrane processes. This is because the effect of concentration polarization (i.e. formation of a boundary layer on the feed membrane surface) is very small compared to that of temperature polarization. As a consequence, MCr allows to produce fresh water from highly concentrated feeds (such as the brine streams) with which RO cannot operate due to the osmotic phenomena. Therefore, the introduction of a MCr unit downstream RO and/or NF retentate, as a post-treatment step, allows to increase the overall recovery factor combined to solid salts production. As a matter of fact, when a MCr follows an RO/NF stage, the highly concentrate brine does not represent waste but rather the mother liquor in which crystals may be obtained.
- The required operating temperature of a MCr is much lower than that of a conventional crystallization operation because it is not necessary to heat the process liquids above their boiling temperatures. Therefore, low-grade, waste and/or alternative energy sources such as solar and geothermal energy can be coupled with MCr systems for a cost and energy efficient liquid separation system.
- MCr is characterized by the separation of the two crucial steps of a crystallization process: the solvent evaporation and the crystallization stage. The evaporation occurs inside the membrane module where the flowing solution is always above its supersaturation condition, while the crystallization occurs inside a separate tank on the retentate line operating in metastable region of supersaturation (Fig. 1). Thus, the crystals produced are expected to show improved size distribution and global quality.
- MCrs are characterized by an axial flux, in laminar regime, of the crystallizing solution through the membrane fibers. This is expected to reduce mechanical stress, to improve the homogeneity of the crystallizing solution and to promote a well ordered organization of the molecules. As a result, crystals exhibiting good structural properties and narrow size distribution are generally produced in membrane crystallization devices.
- Another main feature of the MCr systems is that the membrane does not act simply as support for the solvent evaporation, but it also induces heterogeneous nucleation starting at low supersaturation ratios, depending on the surface characteristics of the membrane.

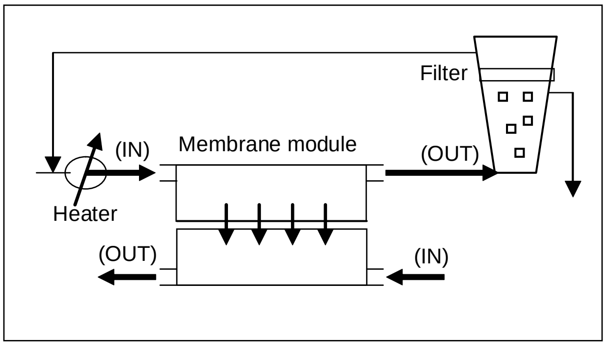

Fig. 1. Schematic representation of MCr technology.

In some previous works, the potentialities of MCr as an avant-garde technique for crystals recovery have been analyzed [2, 3]. In this work, MCr has been used for potable water production and crystals recovery from NF retentate stream of an integrated membrane desalination process constituted by MF/NF/RO.

2. Integrated membrane-based desalination process

The possibility of increasing the recovery factor of the conventional seawater desalination plants has been analyzed by examining the performance of a MF/NF/RO/MCr process. In the considered flow sheet, MF and NF have been introduced for feed water pre-treatment

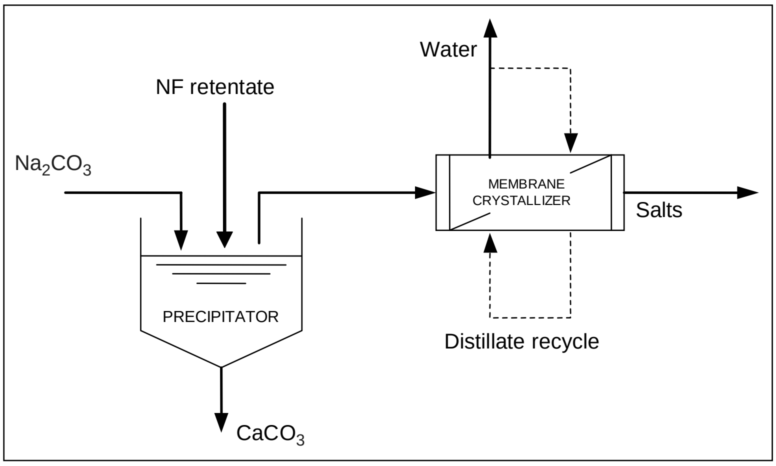

Fig. 2. Schematic flow sheet of part of the lab plant: precipitator (for the removal of Ca^{2+} ions from NF retentate) and MCr (for the recovery of fresh water and salts).

and load reduction to the following RO unit while MCr operates on NF brine in order to increase the quantity of desalted fresh water produced combined to solid salts production. In order to limit calcium sulfate precipitation in MCr operation, Ca^{2+} ions have been precipitated as carbonates by reaction with Na_2CO_3 solutions and, only then, the NF treated retentate stream was sent to MCr operation (see Fig. 2).

In Table 1 the composition of the analyzed feed is reported. The NF acts on the MF permeate with a recovery factor of 75.3%. The RO unit alone gives a water recovery of 40.1%. By introducing the NF unit for the feed water pre-treatment, the RO permeate increases due to the lower osmotic pressure of the water fed to the unit and a global recovery factor of 52% has been obtained. In Table 2, the rejection values and recovery factor of the different units are summarized. Table 3 shows the results of the analyzed flow sheet in terms of product characteristics.

Table 1
Seawater composition.

Ion	Concentration [g/L]
Cl^-	19.00
Na^+	10.50
SO_4^{2-}	2.700
Mg^{2+}	1.350
Ca^{2+}	0.4000
HCO_3^-	0.1420
K^+	0.3800
CO_3^{2+}	0.0035
Br^-	0.0650
Total	34.54

Table 2
Rejection values and recovery factor NF and RO.

Ion	NF [%]	RO [%]	MCr [%]
Recovery factor	75.3	69.06	95.19
Cl	26.7	99.6	
Na	26.7	99.6	
SO_4	93.3	99.6	
Mg	87.7	99.6	
Ca	80.7	99.6	≈ 100
HCO_3	63.3	99.6	
K	26.7	99.6	
CO_3	63.3	99.6	
Br	10	99.6	

Table 3
Product characteristics for the analyzed integrated membrane process.

Brine flow rate [m^3/h]	298.6
Brine concentration [g/L]	91.69
Fresh water flow rate [m^3/h]	751.0
Fresh water concentration [g/L]	0.062
Fresh water recovery [%]	71.4
$CaCO_3$ flow rate [Kg/h]	847.3
NaCl flow rate [Kg/h]	8648.3

In the analyzed integrated membrane-based desalination system, 35.28 kg of salts per cubic meter of treated NF retentate are produced when the MCr works at a recovery factor of 95.2%. Moreover, the presence of MCr on the NF retentate stream increases the recovery factor of the desalination system so much to reach 71.4%, higher than that of a typical SWRO desalination plant (about 40%) and much higher than that of a conventional Multistage Flash (MSF—about 10%).

3. Performance of MCr operations

The crucial requirement for a MCr is to prevent crystal deposition on membrane surface and inside the membrane module. In the lab plant, this problem has been controlled through the following tools:

- by re-circulating the solution in order to remove particles eventually deposited on the membrane surface;
- by continuously recovering the produced crystals through a "crystal recovery system";
- by controlling the temperature of the solution flowing along the membrane module. In fact, the solubility of solids in solution depends on temperature whose effect on salt solubility depends by its enthalpy change of solution. Moreover, it is necessary to consider that, along the capillary module, thermal exchange phenomena between cold and hot streams cause a progressive reduction of temperature, depending on the fluid-dynamic regime. As a consequence, for the salts present in NF retentate (NaCl and magnesium sulfate), a heating guarantees that the temperature of the solution flowing along the membrane is high enough to be always under saturation condition. Through the modeling of the system, it has been calculated that the temperature of the MCr feed must be less than 34°C in order to prevent crystals deposition inside the membrane module.

In Fig. 3, the trans-membrane flux obtained during lab tests at different feed flow rate and constant feed temperature is shown. In both cases, apart an initial transitory stage, trans-membrane flux showed an almost constant trend. The constant trend is characteristic of a good operation because, it means that there are no crystals deposition inside the membrane module. This is because the temperature of feed and the thermal difference between the two streams are high enough to contain the decrease in driving force due to concentration rise. Moreover the slight decrease in the trans-membrane flux observed when the crystals were formed has been solved through a "crystal recovery system". This tool allows to separate the produced crystals from the crystallizing solution.

Moreover, the figure shows that solvent trans-membrane flux enhances when feed flow rate increases. Feed flow rate is an important parameter in MCr operations. It influences both mass and energy transport phenomena: higher feed flow rate means higher Reynolds number and transport coefficients. As a consequence, polarization effects decrease and higher fluxes can be expected.

4. Economical evaluation

An economic evaluation has been made to determine the desalted water cost and the gain for the salts sale for the proposed integrated desalination process. The calculations are based on recent economic data extracted from actual field data and from design studies in literature. All the equations and the assumption to be used for the economic calculations have been meticulously described in [4, 5].

The achieved results through the modeling of the membrane-based desalination system in the case in which:

- the MCr works with a recovery factor equal to 97%, and
- the temperature of the MCr feed is equal to 50°C

are reported in Table 4.

Therefore, the modeling of the integrated system in the specified conditions showed that the desalination system can become attractive also from an economic point of view. However, it should be pointed out that in the proposed flow-sheet with MCr there are also other important advantages:

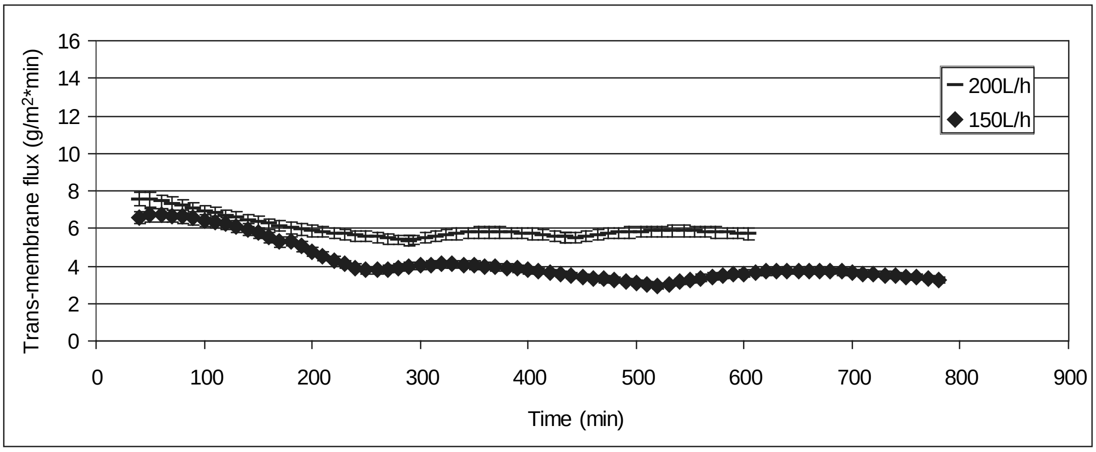

Fig. 3. Trans-membrane flux vs time for tests carried out at different MCr feed flow rate (200 and 150 L/h, respectively) and constant temperature (feed temperature = 34±1°C, thermal difference between cold (permeate) and hot (feed) streams = 16±1°C).

Table 4
Desalted water unit cost and profit for the salts sale for the proposed MF/NF/RO/MCr desalination process [4].

Total annual profit for the salts sale [$/yr]	6,398,000
Total annual cost [$/yr]	4,024,000
*Unit cost[a] [$/m^3]	0.63/0.51[c]
*Unit cost[b] [$/m^3]	−0.44/−0.57[c]

*In the analyzed process a Pelton turbine has been considered as energy recovery device.
[a]Desalted water unit cost without considering the gain for the salts sale.
[b]Desalted water unit cost considering the gain for the salts sale.
[c]If thermal energy is available in the plant or the stream is already at the operating temperature of the MCr unit.

1. *The reduced global size*. In comparison with conventional MSF process, a membrane-based plant is more compact and estate saving. For example, the comparison of a conventional distillation column with a comparable membrane distillation plant shows that the dimensions of the traditional equipment are orders of magnitude larger than those of the membrane plant because the large vapor space required by a distillation column is replaced by the pore volume of a microporous membrane (which is generally on the order of 100 μm thick). Moreover, where conventional distillation relies on high vapor velocities to provide intimate vapor–liquid contact, membrane distillation employs a porous membrane to support a vapor–liquid interface. As a result, the membrane equipment can be much smaller, which translates to a saving in terms of real estate.

   In the case of the membrane crystallizer, the available area between the cold and warm streams of the membrane contactor is also substantially larger than that in the heat exchanger of a conventional crystallizer. In fact, the specific area can be at least 1 order of magnitude higher than those of traditional shell-and tube units [2]. Therefore, the large mass-transfer area offers the possibility of creating a compact contactor with a high surface enclosed in a small volume.
2. *The quasi zero-brine production*. The increase of plant recovery factor allows to produce more fresh water and to reduce the economic and environmental problems related to the brine disposal. These problems are more evident when the desalination plant has to be constructed away from a salt water body. Any existing ground or surface water has to be prevented to the pollution with the salts of the concentrate streams. The transport by pipeline to a suitable disposal point could add up to the total costs.

   Only the use of new parameters consistent with the principles of sustainable growth, such as the ones suggested by A. Criscuoli et al. [6], will give the correct evaluation of the real costs and benefits of the proposed strategy.

5. Conclusion

In this work the potentialities of the MCr for reducing the volume of the concentrate streams usually discharged by the desalination plants have been investigated. In particular, MCr has been used for recovering the water and the salts presents in the NF brine of an integrated membrane based plant constituted by MF/NF/RO. The introduction of MCr on NF retentate stream allowed to increase the recovery factor of the integrated system so much to reach 71.4%, higher than that of a typical SWRO desalination plant (about 40%) and much higher than that of a conventional Multistage Flash (MSF-about 10%). Moreover, 35.28 kg of salts per cubic meter of treated NF retentate are produced when the MCr works at a recovery factor of 95.2%. Special attention has been placed on the stability of the MCr operation by avoiding crystals deposition inside the membrane module and/or on membrane surface. The achieved results are encouraging: the MCr flux was almost constant during all the experimental tests. This means, no crystals deposition inside the membrane module and/or on membrane surface.

In conclusion, adoption of the integrated membrane desalination systems with MCr unit seems to have the potentiality of improving desalination operations, by reducing brine disposal problem and, above all, its environmental impact.

Acknowledgement

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