**The sea as an open sky mine for minerals extraction**

Enrico Drioli1,2, Francesca Macedonio1

*1 Institute on Membrane Technology - National Research Council (ITM–CNR), Via Pietro BUCCI, c/o The University of Calabria, cubo 17C, Rende (CS), 87036, Italy; 2 University of Calabria - Department of Environmental and Chemical Engineering, Rende (CS), 87036, Italy*

*\*Corresponding author:* *e.drioli@itm.cnr.it*

**Highlights**

* Membrane assisted crystallization (MCr) was utilized for brine exploitation.
* New membranes were tested in MCr process.
* MCr performance was analyzed in terms of resistance to wettability and crystals properties.

**1. Introduction**

Membrane assisted crystallization (MCr) is an innovative process which combines crystallization process with membrane technology. This operation uses hydrophobic microporous membranes for promoting solvent evaporation from a feed solution thus concentrating it above its saturation limit and attaining a supersaturated environment where crystals may nucleate and grow. In a membrane crystallizer the membrane matrix acts as a selective gate for solvent evaporation, modulating the ﬁnal degree and the rate for the generation of the supersaturation. Hence, acting on the transmembrane ﬂux, either by changing the driving force of the process or by choosing membrane with proper characteristics, allows controlling the crystallization process very precisely.

**2. Methods**

The description of the lab scale apparatus utilized for performing the tests can be found elsewhere [‎1]. In all the tests, solution was charged in the crystallizer and recirculated through the membrane modules. The membrane-crystallization unit aims to induce supersaturation in solution by removing solvent in the vapour phase. The solvent evaporates at the interface of microporous hydrophobic membranes on the warm (retentate) side, diffuses through the pores and condenses on the opposite (distillate) side. In Table 1 the list of the utilized membranes can be found.

**Table 1.** Membrane utilized in MCr tests.

|  |  |
| --- | --- |
| **Membrane material and configuration** | **Type** |
| Flat sheet Hyﬂon/PVDF composite membrane | AD40H\_010, AD40H\_022, AD40H\_045 |
| Hollow fiber ceramic membranes | CM-L, CM-S |
| Hybrid Bi2Se3/PVDF flat sheet composite membrane | Bi2Se3/PVDF |
| PVDF flat sheet membrane | PVDF |

**3. Results and discussion**

All the tested membranes showed stable performance, without any wetting, during crystallization. Visual observation of the obtained NaCl crystals showed cubic shape whereas the analysis of their crystal size distribution proved their low dispersion (i.e., CV). Moreover, a secondary nucleation was observed which occurred simultaneously with crystal growth due to the contact of the growing crystals with the diﬀerent parts of the plant. This eﬀect was more evident for the membranes with the highest trans-membrane ﬂux due to the highest rate in achieving supersaturation degree, supersaturation rate, nucleation and secondary nucleation. Furthermore, the inclusion of Bi2Se3 fillers in PVDF membranes, assisted the crystal-growth for NaCl, leading to a faster crystal growth and a higher uniformity of the crystal size.

**4. Conclusions**

All the analyzed membranes proved their suitability for MCr process whose performance can be controlled acting on the chemical–physical properties of the membranes and process parameters (temperature, concentration, ﬂowrate, etc.). These aspects would be of undoubted benefit because allow modulating the final properties of the crystals produced both in terms of structure (polymorphism) and morphology (habit, shape, size, and size distribution).

**References**

1. Cui, Z., Li, X., Zhang, Y., Wang, Z., Gugliuzza, A., Militano, F., & Macedonio, F. (2018). Testing of three different PVDF membranes in membrane assisted-crystallization process: Influence of membrane structural-properties on process performance. Desalination, 440, 68-77.
2. Chia-Chieh Ko, Aamer Ali, Enrico Drioli , Kuo-Lun Tung, Chien-Hua Chen, Yi-Rui Chen, Francesca Macedonio. (2018). Performance of ceramic membrane in vacuum membrane distillation and in vacuum membrane crystallization. Desalination, 440, 48-58.
3. Macedonio, F., Politano, A., Drioli, E., & Gugliuzza, A. (2018). Bi 2 Se 3-assisted membrane crystallization. Materials Horizons, 5(5), 912-919.