

Figure 6. A comparative analysis of water consumption in traditional and MCr based mining

Novel membrane processes are being studied for solving future energy, mineral and water crises. Membrane processes such as membrane distillation (MD) and membrane crystallization (MCr) have been evaluated for treatment of challenging solutions such as brine of reverse osmosis (RO) plants and for oilfield produced water [7], [8]. MCr exhibits certain characteristic features that make it superior to the traditional crystallizers: compactness, low coefficient of variance of crystals obtained, improved kinetics and control of polymorph by tuning operating parameters are the main features of interest [15]. Moreover, another aspect of MD and MCr is the potential of treating industrial wastewaters. Wastewater from industrial processes is often considered as a major disadvantage. Often, the wastewater involves additional treatment for meeting environmental requirements for discharge, thus increasing the overall production cost without any gain for the industry. Therefore, novel technologies are interesting for the treatment of difficult wastewater solutions and encountering zero liquid discharge by producing valuable streams for the industry.

A comparison of potentially recoverable minerals from brine of existing desalination plants and their current exploitation through conventional mining has been illustrated in Figure 7 [16]. It can be noted from the figure that amount of Na and Mg in brine from current desalination capacities is more than that obtained through conventional mining. Similarly, strontium and lithium have considerable quantities in brine indicating an attractive opportunity for recovery of these minerals from the brine. The situation will further improve on completion of contracted and planned desalination capacities across the globe.

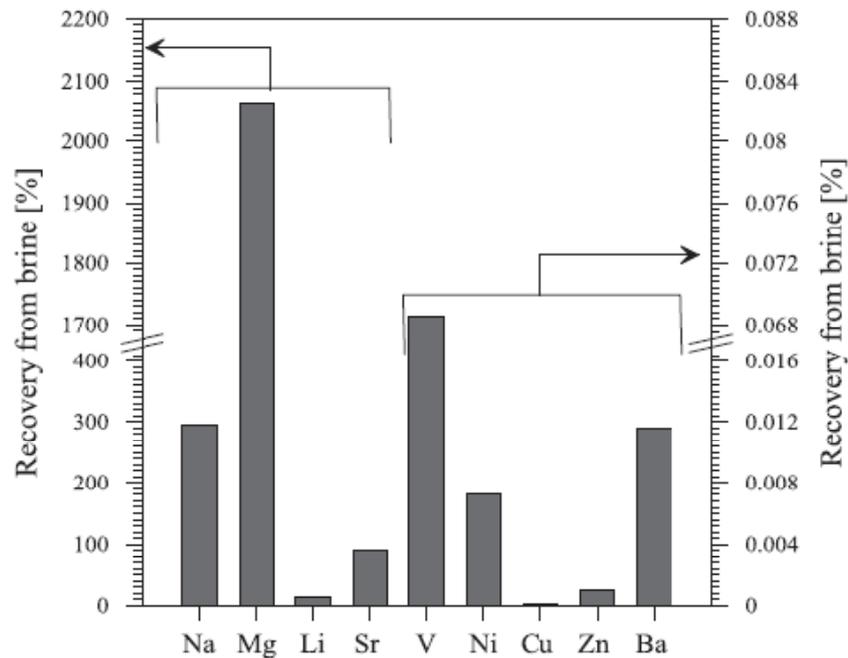


Figure 7. A comparative analysis of potentially recoverable minerals from brine and their quantity obtained through traditional mining.

2. Energy production

Pressure retarded osmosis and RED has been mainly investigated for harnessing blue energy. A rational integration of these processes with other desalination units imparts synergetic effects on performance of both processes. Besides reducing the net energy consumption of desalination processes, these operations also make desalination more clean and green by producing electricity with zero carbon emission and by diluting the concentrated brine which otherwise is a nuisance. The power density can be increased significantly by increasing the brine concentration. In this context, integration of RED with MD can give synergetic effect as demonstrated in a current study [17]

Some interest of applying these technologies for energy production at industrial scale has also been seen recently. The concept of integrating PRO with other membrane operations is gaining attention at industrial scales also. Currently, Applied Biomimetic and partners have setup two pilot plants aiming to generate electricity from geothermal wastewater by using PRO technology (energyforskining.dk/node/8345). The proposed plan is expected to produce emission free electricity while at the same time bringing the salinity level of the geothermal brine low to the permissible limits. Dilution of geothermal brine via PRO will also reduce the corrosion and scaling potential of geothermal stream. Similar concept has been used in Mega-ton project where a pilot plant has been constructed in Fukuoka (Japan). The plant uses 460 m³/d of RO brine which is mixed with 420 m³/day of wastewater. The plant has been able to achieve power density as

high as 13 W/m^2 at 30 bar hydraulic pressure by using commercial hollow fibers from TOYOBO.

Another pilot-scale PRO-hybrid research project has been conducted as the “Global MVP” project in Korea (Figure 8). The objective of this project was to evaluate the feasibility of the RO-MD-PRO hybrid process in terms of reducing the discharged water concentration and the energy consumption. In the hybrid process, the concentrated RO brine enters the MD feed side, and the further concentrated MD brine is then utilized as a PRO draw solution while the waste water effluent is used as the feed solution. Consequently, improvement of total plant efficiency compared to a stand-alone RO plant is expected due to the additional water production by MD and the reduction of net energy consumption resulting from the PRO energy generation. Specifically, the following pilot plant will be built: a RO system capable of $1000 \text{ m}^3/\text{d}$ water production, a MD system with a water production capacity of $400 \text{ m}^3/\text{d}$, and a PRO system having a 5 W/m^2 power density [18]. Recently Statkraft has terminated its activities on power generation through PRO. The company has been operating a prototype of 10kW capacity by applying seawater and river water as draw and feed solution respectively, separated through a membrane with power density of 1 W/m^2 which was far less than economical break-even (5 W/m^2). Although, membranes with power density as high as 10 W/m^2 have been reported in current literature, however, the price and commercial availability of these membranes still remain the unanswered questions. Besides high power density, the appropriate membranes should exhibit high selectivity and minimum reverse solute diffusion. Internal concentration polarization and fouling are the other main issues hindering the performance of PRO process. Due to exposure of support layer to feed solution, fouling and internal concentration polarization issues are more severe in PRO than pressure driven processes. Besides the proper treatment of feed solution, designing and modification of support layer must be emphasized to alleviate this phenomenon.

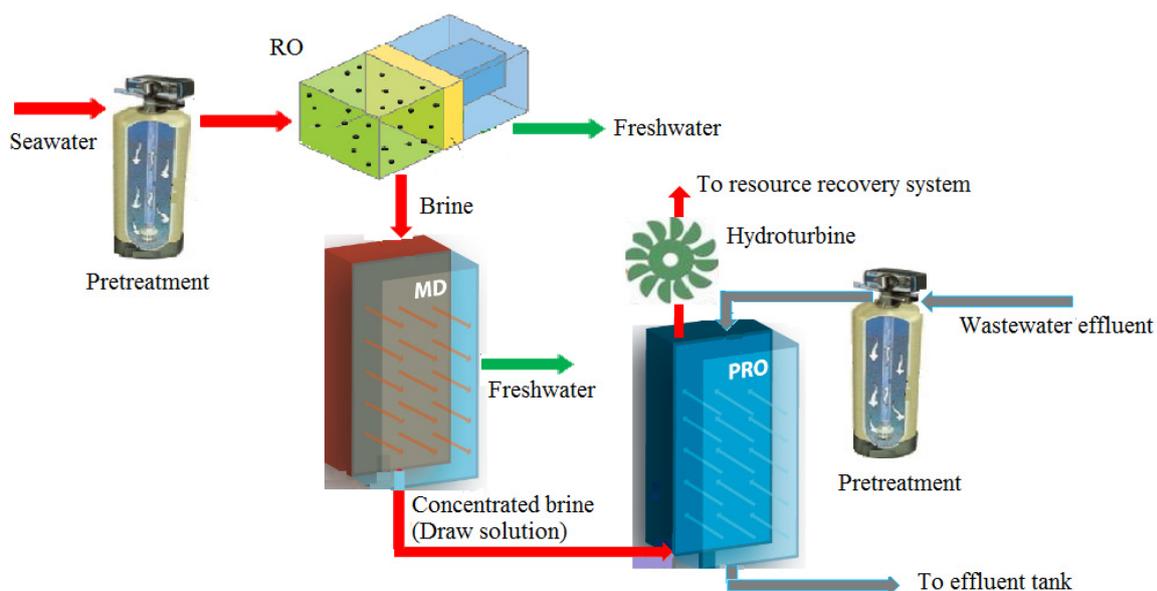


Figure 8: Schematic diagram of hybrid RO-MD-PRO in Korea implemented under Global MVP project.

Conclusion

Seawater is already being exploited to fulfil the demands of freshwater in many countries in the world and might serve as the source to ensure the sustainable supply of minerals and energy in perspective. Membrane operations are expected to be utilized as the main tools to extract these commodities from the sea. The shortcomings of traditional pressure driven membrane processes, largely applied in desalination sector, are being overcome by relatively new processes. Membrane distillation/crystallization has shown promising potential to extract additional freshwater and minerals from seawater/brine. Similarly, PRO and RED have gained attention for energy recovery from the seawater. The development of these processes has been promoted from lab scale to pilot units investigated for potential application in mega projects. However, still a lot of improvements are needed to achieve the techno-economic feasibility of these processes for large scale applications. The availability of suitable membranes for all these processes has been the key challenge. Low fouling (scaling/biofouling) potential, high permeability and long term stability are the common requisite for membranes for all these processes. It can be expected that new materials and techniques will become of increasing importance to incorporate the desired features into membranes. New developments on material fabrication provide interesting perspectives to solve some of these problems [19]. Understanding of transport phenomenon, appropriate module designing and trials at large scale are the other areas to be investigated for practically realizing the true potential of these operations.

Bibliography

- [1] U. Bardi, "Extracting Minerals from Seawater: An Energy Analysis," *Sustainability*, vol. 2, pp. 980–992, Apr. 2010.
- [2] F. Macedonio, C. A. Quist-Jensen, and E. Drioli, "Raw materials recovery from seawater for zero liquid discharge," in *The International Desalination Association World Congress on Desalination and Water Reuse 2015/San Diego, CA, USA*, 2015.
- [3] E. Drioli, A. Criscuoli, and F. Macedonio, *Membrane Based Desalination: An Integrated Approach (MEDINA)*. IWA Publishing, 2010.
- [4] A. Shahmansouri, J. Min, L. Jin, and C. Bellona, "Feasibility of extracting valuable minerals from desalination concentrate: a comprehensive literature review," *J. Clean. Prod.*, vol. 100, pp. 4–16, Aug. 2015.
- [5] J. Veerman, M. Saakes, S. J. Metz, and G. J. Harmsen, "Electrical Power from Sea and River Water by Reverse Electrodialysis: A First Step from the Laboratory to a Real Power Plant," *Environ. Sci. Technol.*, vol. 44, no. 23, pp. 9207–9212, 2010.
- [6] J. Veerman, J. W. Post, M. Saakes, S. J. Metz, and G. J. Harmsen, "Reducing power losses caused by ionic shortcut currents in reverse electrodialysis stacks by a validated model," vol. 310, pp. 418–430, 2008.
- [7] F. Macedonio, C. a. Quist-Jensen, O. Al-Harbi, H. Alromaih, S. a. Al-Jilil, F. Al Shabouna, and E. Drioli, "Thermodynamic modeling of brine and its use in membrane crystallizer," *Desalination*, vol. 323, pp. 83–92, Aug. 2013.

- [8] F. Macedonio, A. Ali, T. Poerio, E. El-Sayed, E. Drioli, and M. Abdel-Jawad, "Direct contact membrane distillation for treatment of oilfield produced water," *Sep. Purif. Technol.*, vol. 126, pp. 69–81, 2014.
- [9] A. Ali, C. A. Quist-jensen, F. Macedonio, and E. Drioli, "Application of Membrane Crystallization for Minerals' Recovery from Produced Water," *Membranes (Basel)*, vol. 5, pp. 772–792, 2015.
- [10] R. Lakerveld, J. Kuhn, H. J. M. Kramer, P. J. Jansens, and J. Grievink, "Membrane assisted crystallization using reverse osmosis: Influence of solubility characteristics on experimental application and energy saving potential," *Chem. Eng. Sci.*, vol. 65, no. 9, pp. 2689–2699, May 2010.
- [11] E. Curcio, A. Criscuoli, and E. Drioli, "Membrane Crystallizers," *Ind. Eng. Chem. Res.*, vol. 40, pp. 2679–2684, 2001.
- [12] C. A. Quist-jensen, F. Macedonio, and E. Drioli, "Integrated Membrane Desalination Systems with Membrane Crystallization Units for Resource Recovery : A New Approach for Mining from the Sea," *Crystals*, vol. 6, pp. 1–13, 2016.
- [13] C. A. Quist-jensen, F. Macedonio, and E. Drioli, "Integrated Membrane Desalination Systems with Membrane Crystallization Units for Resource Recovery : A New Approach for Mining from the Sea," *Crystals*, vol. 6, 2016.
- [14] C. A. Quist-jensen, A. Ali, S. Mondal, F. Macedonio, and E. Drioli, "A study of membrane distillation and crystallization for lithium recovery from high-concentrated aqueous solutions," *J. Memb. Sci.*, vol. 505, pp. 167–173, 2016.
- [15] E. Curcio, A. Criscuoli, and E. Drioli, "Membrane Crystallizers," *Ind. Eng. Chem. Res.*, vol. 40, pp. 2679–2684, 2001.
- [16] C. A. Quist-Jensen, F. Macedonio, and E. Drioli, "Membrane crystallization for salts recovery from brine — an experimental and theoretical analysis," *Desalin. Water Treat.*, vol. 3994, no. November, pp. 1–11, 2015.
- [17] R. Ashu, E. Curcio, E. Brauns, W. Van Baak, E. Fontananova, and G. Di, "Membrane Distillation and Reverse Electrodialysis for Near-Zero Liquid Discharge and low energy seawater desalination," *J. Memb. Sci.*, vol. 496, pp. 325–333, 2015.
- [18] "Global MVP 2013-2018." .
- [19] J. Feng, M. Graf, K. Liu, D. Ovchinnikov, D. Dumcenco, M. Heiranian, and V. Nandigana, "Single-layer MoS₂ nanopores as nanopower generators," *Nature*, pp. 1–4, 2016.