

## Short Note

# Minerals, Energy and Water from the Sea: A New Strategy for Zero Liquid Discharge in Desalination

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Conventional resources of water, raw materials and energy are under extremestress due to rapidly growing population and improved living standards. It has been estimated that more than one billion people on the earth don't have access to the clean fresh water and further predictions indicate that two third of world population will be facing the shortage of freshwater by 2025[1]. Similarly, the speed of mineral extraction is higher than ever for their rapidly growing demand. Several key metals including gold, manganese, platinum, silver and zinc have already been declared as highly depleted in USA. The energy demands are approaching the new figures never observed before. Depletion of fossil fuels has been identified as future challenge. In this context, the finite resources of freshwater, raw materials and energy require implementation of sustainable practices in their exploitation and use.

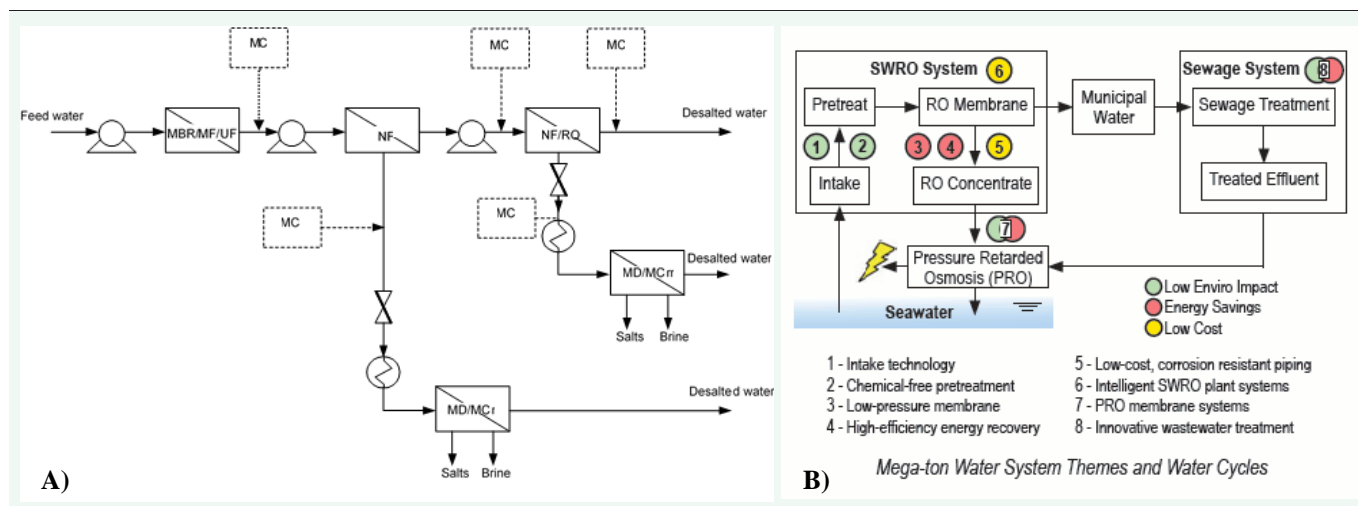
Water, minerals and energy are interrelated and shortage of one influences practices applied in the other. For instance, the shortage of water in mining and energy sector has emerged as a newly realized challenge. The outlook of water shortage in future has constrained the mining industry to look towards alternative water resources and water production methods to meet their increasing demands. The mining industry in major mining countries has been forced by new regulations to use water only produced by the industry itself. These rules have compelled the mining industry to use desalination in order to protect the vulnerable fresh water resources and enhance sustainability in the mining sector [2]. The relation between these three effects raises the question on how long mineral production can be carried out at the speed of the required quantities/qualities at reasonable costs [3].

Although the overall volume of fresh water reservoirs might be enough to fulfill the current demand, unfortunately the distribution of these reservoirs does not match with population distribution across the globe. To address the shortage of freshwater, in many parts of the world, the dependence on

seawater for industrial, drinking and household purposes has greatly increased. Traditionally thermal desalination has been the major applied technique. In many regions of the world conventional thermal desalination plants have been turned into membrane process due to 10-fold more energetically efficient than thermal options [4]. Today, the membrane based desalination processes produce more water than thermal systems. Conventional pressure driven processes, however, face some challenges that need to be addressed, operation at high pressure and the disposal of brine being most significant obstacles that negatively affect the process economy and cause environmental problems.

Due to their high consumption rate, some elements are becoming increasingly scarce. An example of a future possible scarce element is lithium, which is interesting, in particular, for its increasing use in lithium-ion batteries for replacing the fuel dependent transportation system with electrical or hybrid electrical vehicles. Different studies discuss the availability of lithium sources in relation to whether the available lithium in future is able to meet the demand of lithium [5,6]. Lithium compounds are mainly being produced from brines and hard-rock mining. Several drawbacks are attributed to the state-of-the-art lithium recovery such as low lithium grades, low recovery factors, complications in making new production sites or enlarging existing areas for salt lake brines. Furthermore the mining industry is harsh for the environment and associated with high level of pollution. Some drawbacks are also associated with the recovery of lithium from salt-lake brine such as contaminants and separation from compounds such as magnesium due to the similar ionic properties [7].

Recovery of components of interest from waste streams and exploitation of nontraditional sustainable resources are the fundamental keys to realize the objective of sustainable development. For instance, in addition to providing the immense source of freshwater, seawater contains most of the element



**Figure 1** Schematics for MEDINA (a) Mega-ton (b) and SEAHERO (c) projects.

present in periodic table. In addition to the other elements, extraction of lithium from seawater could be an interesting pathway to bridge the gap between demand and supply of this material in perspective as suggested in a recently launched Korean project Global MVP which investigates the lithium recovery by utilizing absorption and lithium battery technology. Research on recovery of lithium from seawater has mainly been focused towards manganese oxide based adsorbents [8]. Supported liquid membranes might also be a potential lithium extractor from seawater [9]. However, the main issue for these technologies is the extraction at the low concentration contained in seawater at efficient rate and reasonable economic expenses.

Due to their less energy intensive nature and excellent potential of separation and purification, membrane processes (standalone or integrated with conventional processes) may provide an interesting pathway to recover valuable components from non-conventional sources. Recovery of strategic elements from seawater by using membrane operations may require the treatment of highly concentrated brine. With progress in membrane technology, new membrane operations are emerging offering the possibility to overcome the drawbacks of conventional membrane processes. For example, membrane distillation (MD) is a new membrane process based upon the vapor pressure gradient created across a microporous hydrophobic membrane. In contrast to RO which cannot be operated to go beyond a certain recovery factor, MD offers the possibility to concentrate the solutions to their saturation level. The combination of MD and well established operations for desalination offers highly interesting opportunities [10]. Actual experimental data suggests that, if MD is operated on RO retentate, the total amount of desalinated water represents almost 88% of the feed water. Additionally, the use of a Membrane Crystallization (MCr - an extension of MD concentration up to supersaturation) allows extracting not only the water but also the minerals contained in the brine streams. MCr offers some important advantages with respect to conventional crystallization processes such as: well-controlled nucleation and growth kinetics, fast crystallization rates and reduced induction time, membrane surface promoting heterogeneous nucleation and control of supersaturation level

and rate, possibility to produce specific polymorphs [11]. The technical feasibility of recovering NaCl, MgSO<sub>4</sub> and CaCO<sub>3</sub> has been established at lab scale and further investigations for lithium and strontium recovery are in progress. In addition to MD, the application of forward osmosis (FO) may also become interesting in perspective to reduce the desalination cost even for challenging solutions. Similarly, the use of reverse electro-dialysis can become interesting for treatment of concentrated salt solutions. MD also offers the possibility to concentrate the draw solutions used for FO process applied for desalination and other similar objectives. The integration of pressure retarded osmosis or reverse electro-dialysis for energy production from salinity gradient, with further water production thanks to RO systems and metal salts concentration and crystallization from their brines might be a strategic intensified industrial sector in future time.

To address the challenges associated with the shortage of water, energy and raw materials, the process industry needs to be redesigned in accordance with guidelines of process intensification strategy (PIS). Modern membrane engineering represents one of the possible and the most interesting ways for developing processes coherent with PIS to meet the challenges of the modern world. Membrane engineering at present is providing interesting solutions to some of the major problems of our modern industrialized society for decreasing the energy consumption, resolving the environmental concerns and exploring the potential of many processes in a better and improved way. In food industry, the membrane operations are becoming of significant importance to concentrate the products and to treat the waste streams. For wastewater treatment, conventional activated sludge plants have been turned into membrane bioreactors due to their compactness (up to 5 times more compact than conventional plants), reduced sludge production and considerable level of physical disinfection. Similarly in energy sector, the innovative concepts such as pressure retarded osmosis and reverse electro-dialysis are emerging to achieve the sustainability and to tackle the problem of CO<sub>2</sub> emission.

The concept of energy production and mineral recovery

from desalination process opens an interesting gateway to reduce the overall cost of the process. Recent progresses in MD and MCr have well identified their potentialities. National and international programs have been also suggested for accelerating, on large pilot scale plants, the potentialities of this strategy. An example can be found in the European research project MEDINA [12], in the Megaton project in Japan and in the SEAHERO project in South Korea. MEDINA project aims to improve the membrane based desalination in terms of water quality, recovery factor, production cost and brine disposal impact by using integrated approach (Figure 1a). The objective of Mega-ton project is to develop environmental friendly, cheap and energy saving water treatment technologies. As shown in Figure 1(b), the project incorporates the use of better pretreatment techniques and pressure retarded osmosis (PRO) to reduce fouling and to harness energy, respectively. The basic concept of SEAHERO project shown in Figure 1(c) is the similar. In first part of the project; the emphasis has mainly been on increasing the desalination capacity while the second part addresses the brine disposal issues. Hybrid systems with membrane distillation and pressure retarded osmosis units are proposed for the extraction of valuable resources from the brine, the minimization of the environmental impact of the brine and the recovery of energy. Moreover, the SEAHERO project has suggested a hybrid system forward osmosis/reverse osmosis for increasing the recovery factor by 30 % and hereby reducing the brine volume in the same extend. This hybrid desalination process can minimize the energy consumption to less than 2.5 kWh/m<sup>3</sup> and water price to 0.6 \$/ton.

For successful commercial implementation of innovative membrane processes (MD/MCr and PRO) in these projects, several challenges have to be overcome. The membranes used for MD/MCr must exhibit and retain a strong hydrophobic character to avoid the wetting phenomenon that depreciates the process performance and product quality. Thermal polarization should be minimized to avoid the thermal losses associated with the process. Similarly, salt scaling occurring at the membrane surface and within the pores should be controlled by improving the process and membrane features. The fabrication of appropriate membrane module is another challenge that needs to be addressed [13]. Similar to MD, the availability of suitable membranes that allow the passage of water at adequate rates is a challenge. Internal concentration polarization (ICP) occurring in the support of layer of membrane limits remarkably water flux and associated power density. The new generation of cellulose acetate membranes originally developed for forward osmosis is capable to decrease ICP. The unavailability of robust and fouling resistant membranes with minimum internal concentration polarization and fouling tendency are the main obstacles for economical commercialization of PRO process.

To summarize the discussion, redesigning of process industry in accordance with guidelines of PIS is necessary to achieve sustainability in field of water, energy and raw materials. The use

of less adopted techniques, practices and resources may become necessary in perspective to address the new challenges. In this scenario, membrane operations have an important role to play. However, successful and sustainable application of membrane operations for simultaneous recovery of freshwater, energy and mineral, several challenges have to be addressed. The availability of appropriate membranes for PRO, reverse electro dialysis and MD/MCr is still challenging. Better control of membrane properties through improved manufacturing and new membrane materials has to be realized. The control of biofouling is necessary to ensure the long life time of membranes. Similarly, a better understanding of mass transport phenomenon and proper module design are crucial. The large scale experimental set-ups should be designed and operated to understand the challenges related with practical implementation of the technology.

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