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Water, Energy and Minerals from the Sea

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ABSTRACT

Conventional sources of freshwater, energy and raw materials are facing the risk of depletion due to rapidly increasing population and improved living standards. To ensure the sustainable supply of these commodities in adequate quantities in future, their alternative sources must be exploited. Seawater is an interesting candidate in this context. Besides providing fresh water, seawater offers the possibility to extract more than sixty elements contained in it. Membrane operations offer technically viable routes to achieve these objectives. New developments in membrane technology also offer exciting perspectives to harness energy by exploiting the salinity of this water. Reverse osmosis (RO) has been widely practiced for freshwater production from seawater while membrane distillation/crystallization has been evolved as an interesting candidate to recover additional freshwater and minerals from brine coming from seawater desalination installations. Besides fulfilling the current demand of traditional minerals such as sodium, magnesium etc., the brine from the global desalination capacities has the potential to provide significant fraction of total consumption of strategic elements including copper, lithium, molbidinium, uranium and cesium. Similarly, the application of pressure retarded osmosis and reverse electrodialysis allows generating clean energy from seawater that can contribute significantly in lowering the dependence on carbon based fuel. However, to realize the commercial applications of less explored membrane operations, more initiatives at research and development level are required. Development of more specific membranes, better understanding and control of transport phenomenon, improvements in module designing, control of scaling and fouling (particularly biofouling) and minimization of internal concentration polarization

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(for PRO) are the main challenges to be addressed to guaranty the successful implementation of these processes at large scale.

1. Introduction

The world's population has crossed the figure of seven billions and is still growing at significantly high rate. Booming population combined with increased gross domestic production has stressed the conventional resources of material utilities and energy. Consequently, the conventional resources of raw material and energy are following the depleting trends. For instance, the access to portable water in adequate quantities is one of the biggest challenges of this century. The current world's population consumes almost 45,00 km^3 of freshwater annually for domestic (10%), agricultural and industrial purposes (20%). It has been stated by UN that world would require 30% more water between 2012 and 2030. Precise predictions say that 30-40% of world's population will be facing water scarcity issue by 2020. Disturbed weather patterns in different parts of the world can further worsen the situation. To fulfill the increased food demands of the world, the agriculture sector is expected to grow at high pace that will result in more water consumption. State-of-the-art practices for freshwater production have not been able to match the requirements imposed by ballooning population and nourishing economies. As shown in Figure 1, the most part of the water consumed today is coming from the conventional sources of freshwater. Desalination has appeared and grown at more than exponential pace but has been unable to bridge the gap between demand and supply of freshwater.

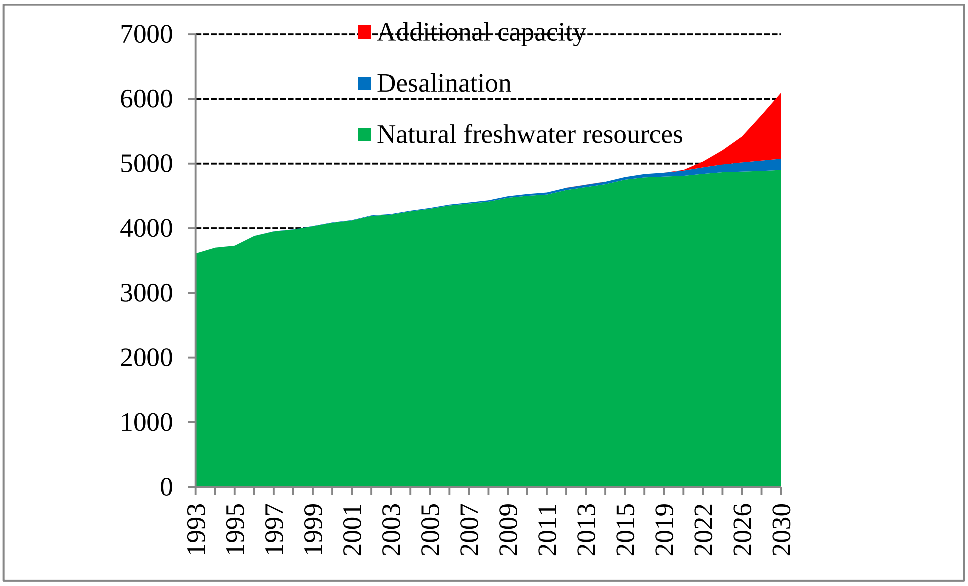

Figure 1: Water availability and demand from various sources

Similar to the water, sustainable development across the globe is highly dependent on an adequate supply of minerals from the mining industry. Likewise other industries, mining sector must adopt and practice more sustainable extraction methods and procedures. Water scarcity, high energy cost and depletion of strategic minerals are driving the interest for innovation in mining sector in today's world. With maturity of a mine, the quality of ore might degrade leading towards more consumption of energy and water. At the same time, population increase, climate changes, and ongoing industrialization are also putting pressure on water, energy, and minerals. It has been calculated that with current consumption of resources, an equivalent of two planets would be required by 2050 to ensure the adequate supply of resources. These resources are, moreover, limited and cannot be used without any concern. A strong nexus between water and raw material production exists and the effect of water stress on mining sector can be clearly realized. The mining industry has been forced to minimize the water consumption from existing resources or contaminate the existing water resources, and at the same time not to threat the water supply of the local community. Use of water in mining is becoming a hot topic for debate and countries like New Zealand have already restricted mining activities to preserve their environment and water resources. Due to extreme stress on extraction and decrease in production efficiency of existing mines, energy consumption has grown rapidly in the last decades and is projected to increase further in the following years [2]. Therefore, the conventional mining industry needs revolutionary changes to cope with the challenge of sustainability.

In order to exploit the alternative and sustainable resources of raw materials, seawater can serve as a source for mineral extraction. Most of the elements present in the periodic table exist in the sea, thus sea can serve as ''open sky mine''. Moreover, as an interesting and positive side effect, it can contribute to the conventional mining industry and hereby reduce mineral depletion. Historically, mining from the sea was considered during the oil crisis of the 1970. Yet, it never reached breakthrough due to several deficiencies, including high cost, low efficiency, lack of technological development, etc. In reality, the proposed strategy of direct recovery from seawater is difficult and might still be an impossible task. However, its feasibility has improved much more than 1970s due to new technological developments, higher risks of mineral depletion, requirements of sustainable water and energy sources. Today some minerals are already being extracted such as Na^+, Mg^{2+}, Ca^{2+}, K^+ [1]. Several research activities have been carried out to extend the number of ions to be recovered from seawater [1]. The ocean has in general much greater content in comparison to mineral resources on land [1], [2]. The economic feasibility of mining from sea further improves when simultaneous water, energy and mineral extractions are considered as proposed in European funded project MEDINA [3] and Global MVP project. The problem of low concentration of ions in seawater can be partly addressed when considering the use of brine from desalination processes combined with advanced separation processes with capability of concentrating the solution to very high level. Shahmansouri et al. have highlighted some of the potential profitable elements which can be recovered from RO brine ([4]. Besides the conventional minerals, strategic and rare elements such as cesium, uranium, rubidium, cesium, lithium, strontium etc. can become feasible in future due to technological improvements in extraction processes and due to their depletion from conventional mining sources.

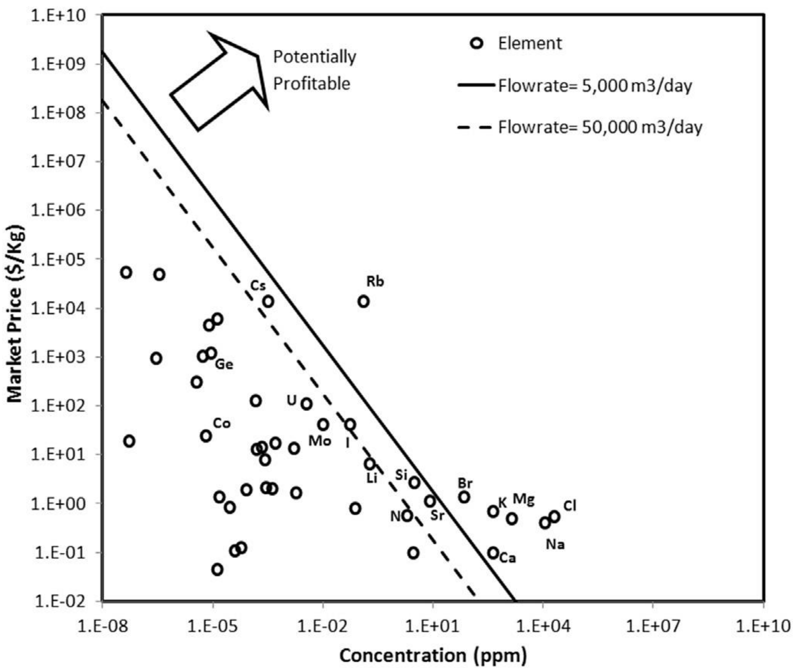

Figure 2. Potential profitable minerals that can be recovered from RO brine [4].

Besides water and raw materials, the oceans also provide the opportunity to harness clean and sustainable energy. Salinity gradient energy (blue energy) is an osmotic energy obtained by mixing two solutions with different level of salinity. It is a completely renewable and sustainable energy with a total global potential of about 1.4 - 2.6 TW out of which ~980 GW is extractable depending on the employed technology [5][6]. It has been estimated that this amount of energy would be sufficient to fulfill around 20% of worlds current energy demand. At the same time, it would decrease our reliance on carbon based fuels for energy production.

2. Membrane technology for water, minerals, and energy production from the sea

2.1 Water and minerals recovery

Among the technological options available today, membrane technology represents the most interesting solution to recover water, energy and minerals from the sea. Membrane engineering is aligned with sustainable development, which has become important for many industrial processes. Membrane engineering, through the process intensification strategy, can redesign conventional process engineering with applications in several industrial processes; e.g., wastewater treatment, desalination, and many other applications where separation is needed [3]. Membrane engineering meets the goals of PIS for several reasons, including high selectivity and permeability for transport of specific components, ease of integration with other processes or other membrane operations, less energy intensive, high efficiency, low capital costs, small footprints, high safety, and operational simplicity and flexibility [4–7].

Significant success has been recorded in successfully utilizing membrane technology in desalination sector. Today's desalination industry has widely adopted reverse osmosis (RO) for its less energy intensive nature, compactness and safer operation. Thermal processes are being practiced only in the regions with abundant sources of petroleum based fuels. Despite of all technological improvements, the pressure driven processes have certain characteristics still to be improved: operation at high pressure, high energy consumption, utilization of high grade energy, limited recovery factor (typically 40-50%) and disposal of brine are the most significant obstacles that negatively affect the process economy and cause environmental problems. 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]. New processes such as pressure retarded osmosis (PRO) and reverse elctrodialysis have the potential to generate clean energy from seawater. The use of the new processes in integration with the traditional ones can not only resolve the problem of waste handling but also provides the opportunity to boost the economy of the process. Integrated approach takes into account energy saving (also production in certain cases), water rationalization, minimization of chemical utilization, resource recovery and waste production [4]. Therefore, integrated systems can contribute significantly to the solution of strategic aspects of industrial productions. Different membrane operations can be coupled in integrated systems for approaching the ambitious objective of "zero liquid discharge". One example has been shown in Figure 3.

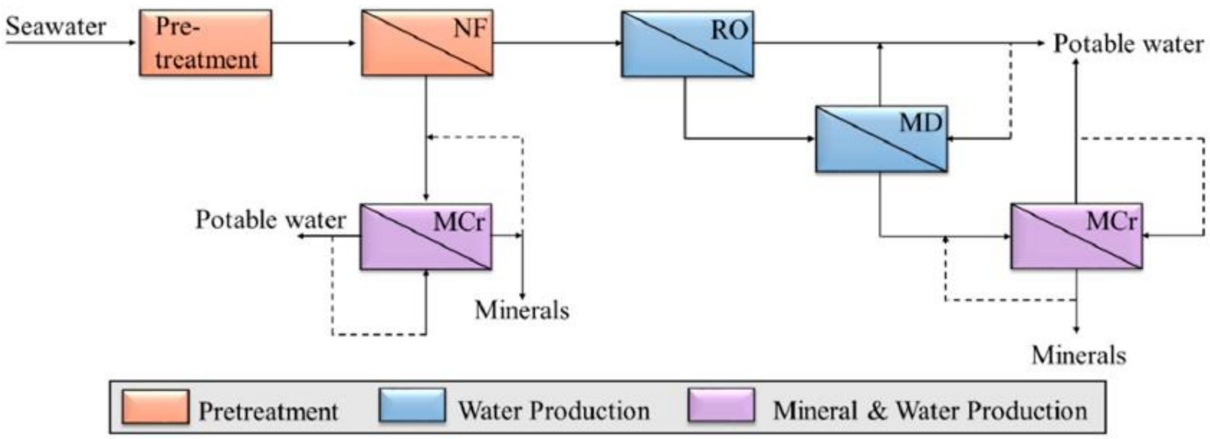

Figure 3. One of the flowsheets for minerals recovery from seawater by using MCr

Simultaneous minerals and water recovery by using MD/MCr has been the subject of some of the recent research efforts[9]–[12]. The recoveries from NF and RO brine have been studied [13]. NF serves as the pretreatment for RO as shown in Figure 3. The concentration of various ions in NF and RO brine becomes significantly higher than the corresponding concentration in starting solution. A typical case has been shown in Table 1. Typical recovery rates for RO and NF were considered as 52 and 75.9%, respectively. The amount of freshwater and minerals that can be recovered from NF retentate by applying MD/MCr has been shown in Figure 4. $BaSO_4$ and $SrSO_4$, which find applications in oil and gas drilling, precipitate initially. As shown in Table 1, the concentration of these compounds in sea water is very low; however, considering the mega desalination projects in future with capacities in range of millions of cubic meter per day, the overall quantity of these minerals can become attractive. However, the better control of crystallization process and associated separation of various compounds needs further attention to ensure good crystal quality in terms of purity.

Table 1. Concentration of different ions in seawater, NF and RO retentates

Element	Seawater Concentration (ppm)	NF Rejection	RO Rejection
Barium Ba	0.021	87.7	99.6
Chlorine Cl	19400	26.7	99.6
Cesium Cs	0.0003	87.7	99.6
Copper Cu	0.0009	87.7	99.6
Potassium K	392	26.7	99.6
Lithium Li	0.17	26.7	99.6
Magnesium Mg	1290	87.7	99.6
Manganese Mn	0.0004	80.7	99.6
Sodium Na	10800	26.7	99.6
Nickel Ni	0.0066	87.7	99.6
Rubidium Rb	0.12	26.7	99.6
Sulfate SO4	2708	93.3	99.6
Strontium Sr	8.1	87.7	99.6
Uranium U	0.0033	40	99.6
Zinc Zn	0.005	26.7	99.6

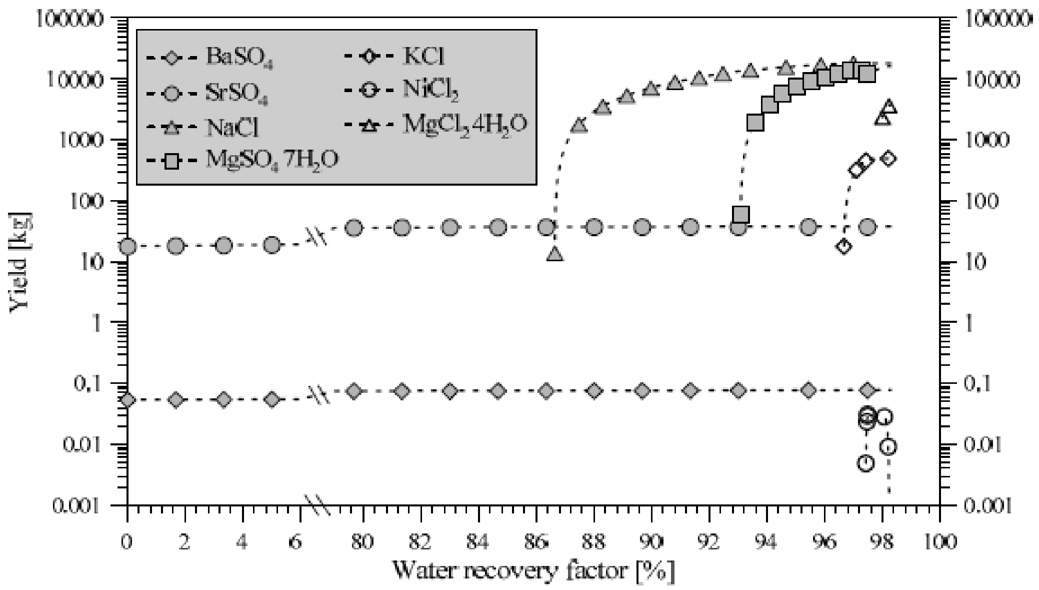

Figure 4. Amount of freshwater and minerals that can be extracted from NF brine

The extractable minerals form RO brine, as function of water recovery factor, have been shown in Figure 5. The figure also includes most of the minerals extractable from NF retentate. However, due to retention of monovalent ions by RO membrane, the order of precipitation changes. NaCl starts to crystallize first and ions like strontium, magnesium and barium are difficult to precipitate from RO brine. The figure also indicates that application of MCr at RO retentate allows recovering LiCl which has high strategical importance due to its increasing use in Li batteries. Recovery of LiCl from a single salt solution has recently been demonstrated experimentally [14]. The study indicates that it is possible to recovery two polymorphs of LiCl depending upon the operating conditions applied. However, it was demonstrated that widely practiced DCMD configuration is not capable to reach the concentrations high enough to guarantee the precipitation. VMD was found to be the feasible configuration for LiCl recovery.

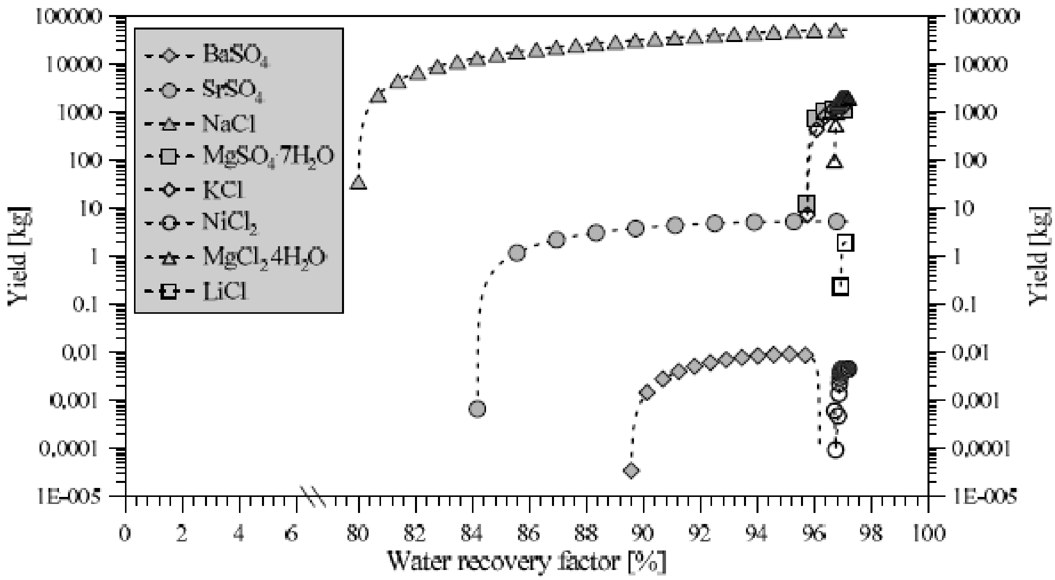

Figure 5. Ions extractable from RO brine by applying MCr

As stated in section, a side-advantage of minerals recovery from brine is the reduction in use of water requirements. A comparative analysis of water consumption in traditional and sea mining has been illustrated in Figure 6. Use of water in mining industry is essential to perform several functions including minerals processing, dust suppression, slurry transport etc. Despite of significant efforts from mining industry in this direction, the overall water consumption is still very high. MCr, on the other hand, offers overall water production rather than consumption. It can be seen from the figure that in case of Ni, the amount of water produced through MCr is much higher than the corresponding consumption through traditional mining industry.

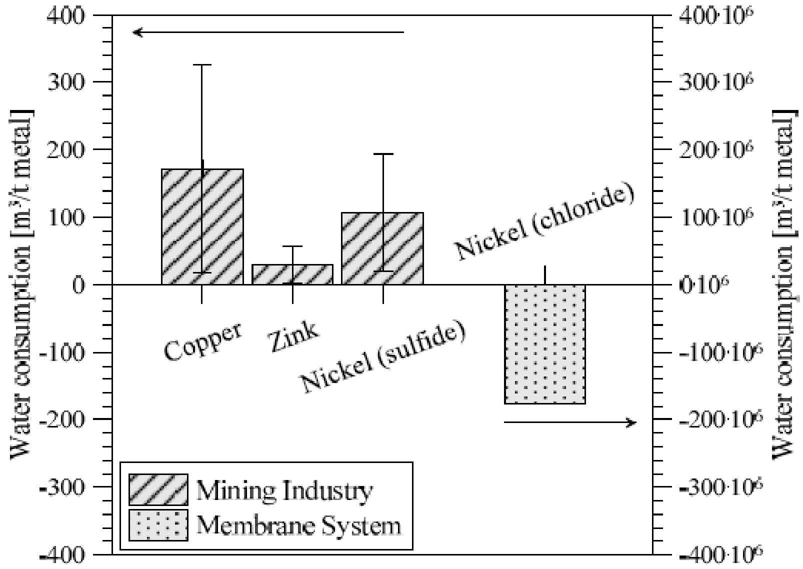

Figure 6. A comparative analysis of water consumption in traditional and MCr based mining

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.

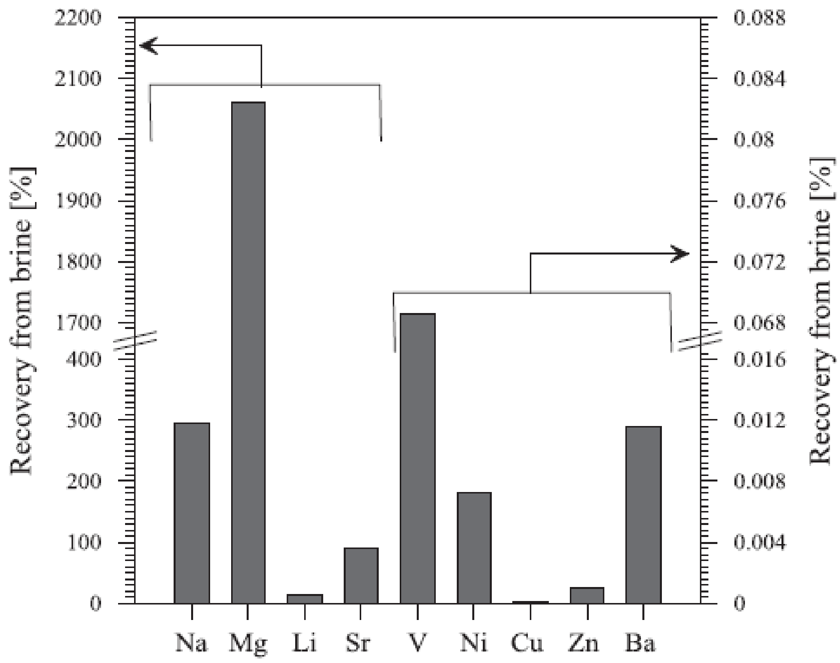

Figure 7. A comparative analysis of potentially recoverable minerals from brine and their quantity obtained through traditional mining.

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 m^3/d of RO brine which is mixed with 420 m^3/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 m^3/d water production, a MD system with a water production capacity of 400 m^3/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.

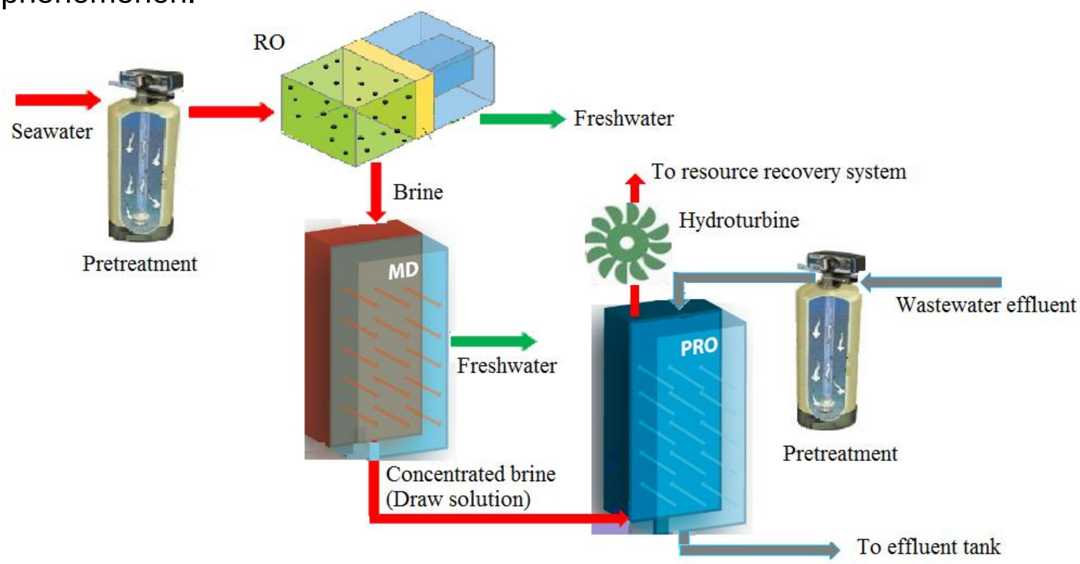

Figure 8: Schematic diagram of hybrid RO-MD-PRO in Korea implemented under Global MVP project.

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 form 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 available 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.

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