IWC 22-34

# New Approaches for Membrane-Based Ocean Mining of Sodium Chloride for Chloralkali Feedstock

CRAIG R. BARTELS PhD AND RICH FRANKS, P.E.
Hydranautics
Oceanside, CA

ELI OKLEJAS AND RORY WEAVER
FEDCO
Monroe, MI

:

KEYWORDS: brine concentration, ultra-high-pressure-RO, ocean brine mining, turbo

## ABSTRACT

Due to the growing scarcity of minerals from traditional mining sites, some coastal countries are turning to the potential benefits of recovering minerals from the ocean. This is actively being pursued in Saudi Arabia, where new treatment schemes are being developed to economically achieve this goal. This paper will report on testing and evaluation of novel membrane processes with 4 different membrane types to maximize the recovery of minerals from seawater at a pilot site in Jubail, KSA. The novel process utilizes a variety of membranes, including softening nanofiltration, seawater reverse osmosis (SWRO), ultra-high-pressure RO (UHP-RO), and brine concentration membranes. The pilot also demonstrates the benefit of using multiple turbochargers that can be linked together to recover energy more efficiently while precisely controlling the boost pressure to each stage of the high-pressure RO system. The pilot data proves that the system can make all three desired products at high quality and at relatively low energy and capital costs. Initial results indicate that the brine from the UHPRO can reach TDS values as high as 100,000 mg/l, while the combined RO permeate was 700 mg/l TDS. This process will be the basis for a 53 mgd (200,000 m3/d) commercial treatment system that will supply concentrated sodium chloride brine to the Saudi chloralkali industry.

# INTRODUCTION

Conventionally, minerals have been mined from the earth through surface or subterranean mines. In some exceptional cases, minerals have been recovered from highly concentrated brine solutions, such as from deep brine wells or brine seas, such as the Dead Sea or the Great Salt Lake. In most of these cases, the highly concentrated brine solutions help improve the economics of mineral recovery. In some cases, minerals have been recovered from ocean water, but this usually entails spreading water over a large area to allow solar evaporation to do the concentration of the minerals. The inherent limitation of recovering minerals from ocean water is the high energy required for conventional evaporators and crystallizers or the long time needed for solar evaporation. These are effective but have both high capital and/or operating costs (Saltworks). Thus, engineers have desired to implement more cost-effective membrane technology in the concentration steps, but conventional SWRO cannot go much beyond 75,000 mg/l of TDS, which still leaves much water in the brine that needs to be removed. Figure 1 shows the relative cost of treatment as a function of water salinity for RO and evaporators.

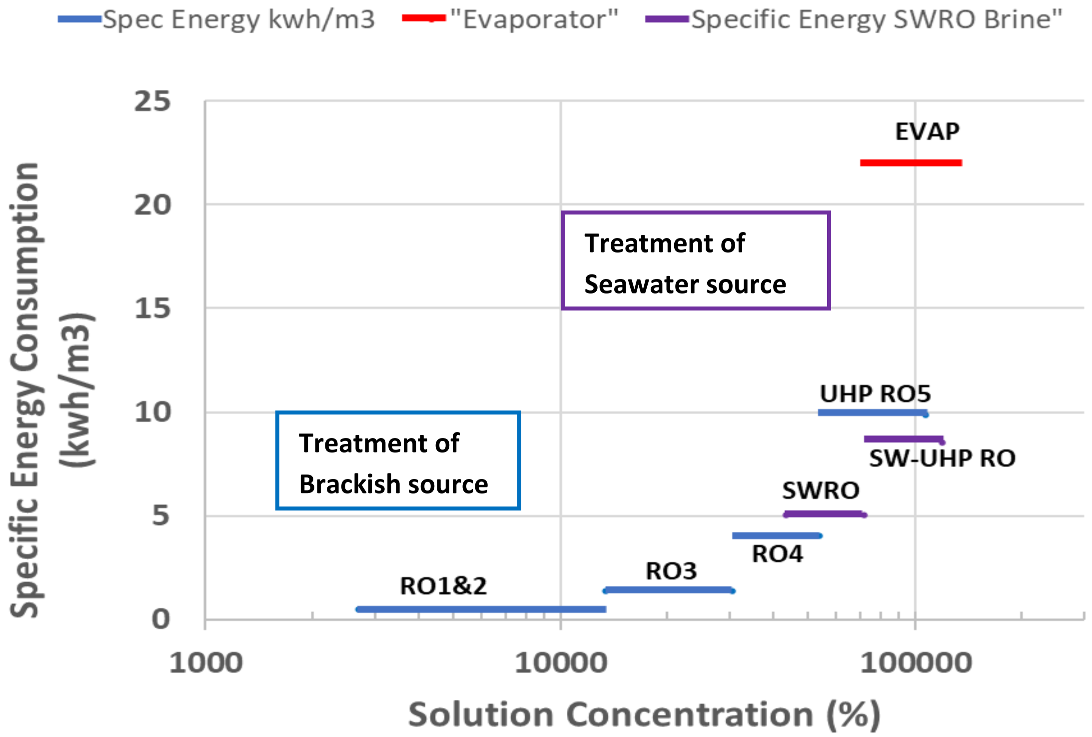


Figure 1 Specific Energy for concentrating a range of feed salinities with RO and Evaporators (Saltworks)

Over the past few years, however, the Desalination Technology Research Institute (DTRI) in Saudi Arabia, has been developing a novel process that utilizes new membrane technology to highly concentrate ocean water with membranes while minimizing the need for evaporators. The primary target would be to recover sodium chloride for use in their chlor-alkali industry, which depends on a surface mine that will soon be depleted. In addition to this salt, there is also a desire to recover other valuable minerals, such as Mg, Br, and others. A preliminary estimate of minerals that could be economically recovered from seawater by such a novel process is shown in Figure 2.

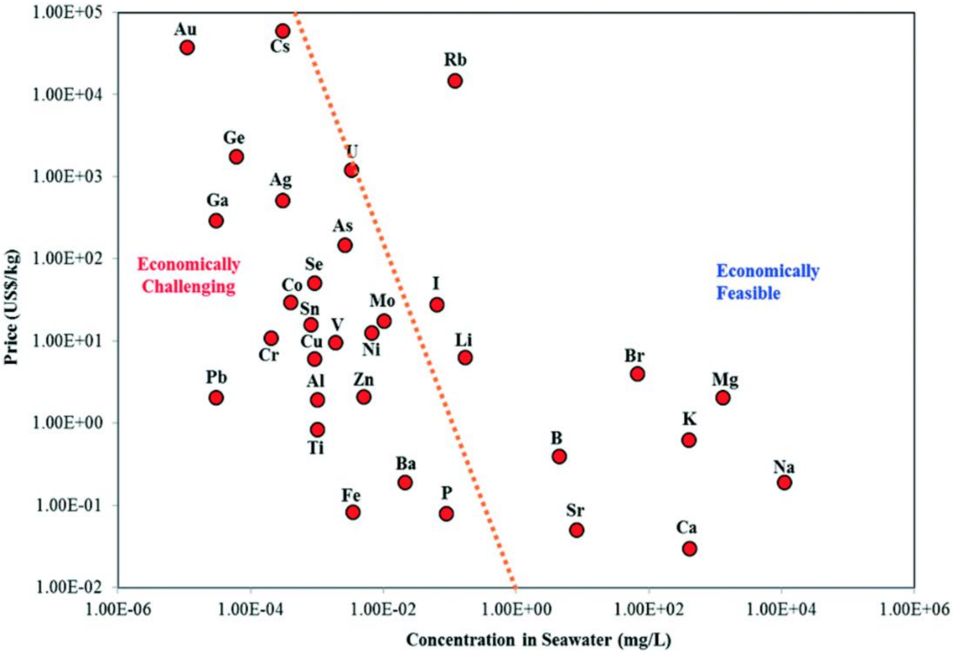


Figure 2 Selling price of current minerals versus their concentration in seawater (Voutchkov 2022)

The process being developed is based on the conventional use of SWRO, which is a main source of potable water in Saudi Arabia, but with the addition of other key treatment steps. Since there is a significant amount of SWRO brine available in Saudi Arabia, it is the perfect source for ocean mining. However, treating this SWRO brine by additional membrane processes has many challenges due to the high concentration of scaling minerals present in the brine. Novel treatment steps are being proposed to manage these new challenges.

New membrane technology being considered for ocean brine mining will likely include softening nanofiltration, UHP RO and new brine concentration membranes to further concentrate SWRO/UHP RO brine to 22-25% salt. These new technologies are already being piloted at a site in Jubail, KSA, and this paper will present the results of that pilot as well as assessment of new technologies which will soon be piloted.

## NOVEL PROCESS DESIGN FOR OCEAN BRINE MINING

The conceptual design of the institution's membrane treatment process is shown in Figure 3. The concentrated brine from the last stage would be treated by specialized crystallizers to recover the NaCl for use in the chlor alkali industry and bromide (Br) for the oil industry. Essentially, there are three main product streams which result from the process, the Mg rich brine, potable stream and the monovalent rich brine stream. These would all be key revenue generating streams. To achieve the quality of water required from this process, the permeate from the brine concentration membranes is recycled back to the SWRO stage. We will next consider the individual treatment units: Low Pressure Nanofiltration (NF), SWRO/UHP RO, and Brine Concentration (BC).

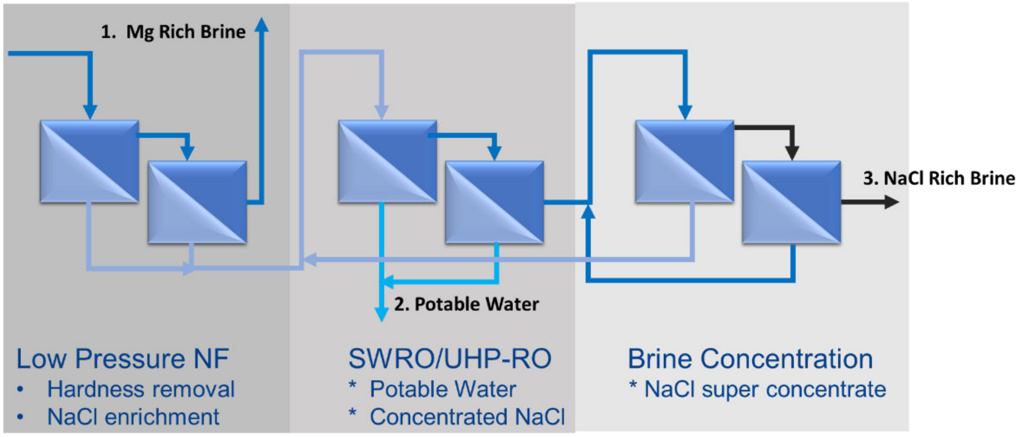


Figure 3  Novel treatment scheme being developed to harvest valuable minerals from seawater.

A pilot plant was designed to demonstrate this process on seawater from the Arabian Gulf near to the Jubail site on the east coast of Saudi Arabia.  FEDCO procured the pilot and designed/provided the energy recovery devices, while Hydranautics supplied the NF and RO membranes as well as the design information to optimize the membrane process.  The operating site at the institution's lab, also provide key input to ensure the system integrated smoothly with the plant.  Engineering staff from all three entities were present and supported commissioning and start-up.  The design of the pilot is shown in Figure 4.  The NF system comprises a low-pressure pump, 2 stages of NF and a separate cleaning system.  The NF permeate is collected in a holding tank and used to feed the SWRO stage.  A key feature of this RO stage is the use of two separate turbochargers which optimize membrane performance and energy recovery.  This technology, called BiTurbo™ is ideally capable to boost and control feed pressure to both the SWRO and the UHP RO stages.  Due to the high efficiency of the turbo, there is sufficient energy to raise the pressure to the UHP RO stage to reach the design flux, but with residual pressure which then powers the first stage turbo, providing a portion of the required energy needed to reach the design flux in the SWRO.

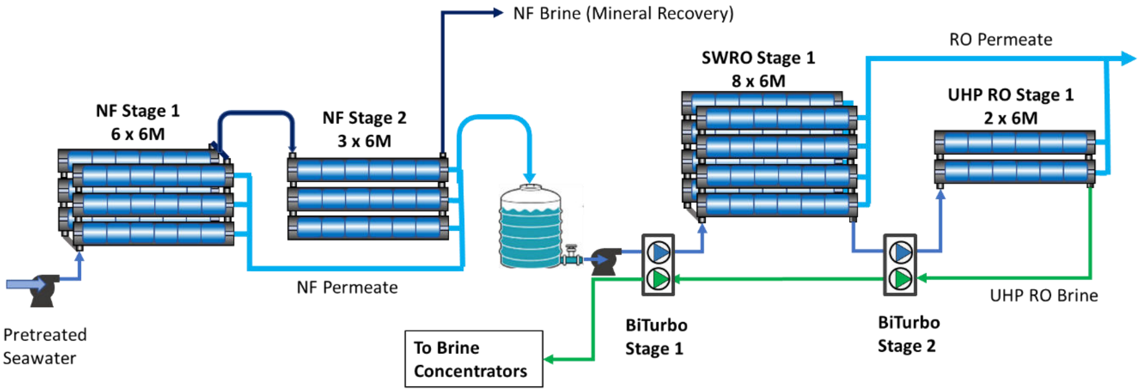


Figure 4  The NF/SWRO/UHP RO pilot at Jubail used to demonstrate the capability for a high recovery membrane system to lower the cost of ocean brine mining

The NF portion of the pilot was housed in one shipping container, while the SWRO and UHP RO were in a second container. A view of the latter is shown in Figure 5, along with a picture of the two turbos.

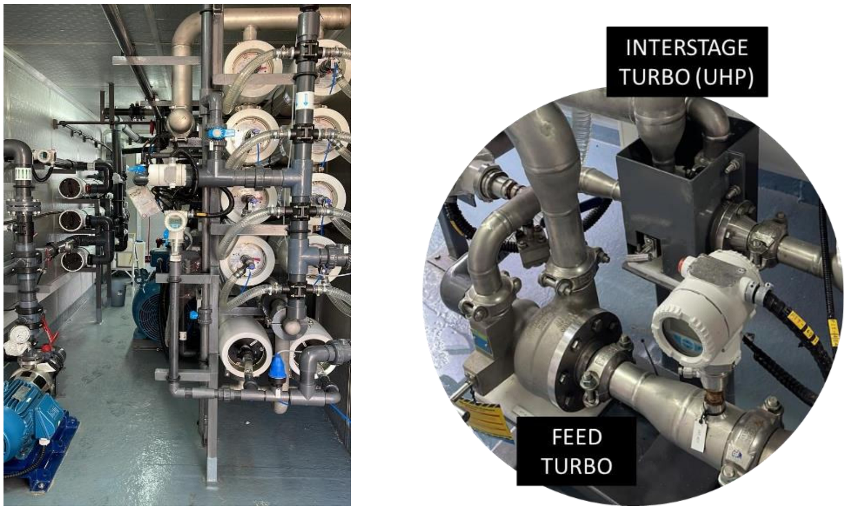


Figure 5 View of the SWRO/UHP RO container and the two turbos used to boost pressure and recovery energy from the brine.

LOW PRESSURE NF - In order to highly concentrate seawater, the first step must be the conditioning of the water to remove/reduce the scaling ions in the water, namely Mg, Ca, and SO4. This can be effectively done with sulfate selective nanofiltration. These novel membranes have unique capability to selectively remove divalent anions and cations, while passing most of the monovalent ions. Thus, these NF membranes would be used to treat the raw seawater, with the monovalent-rich permeate being fed to a SWRO process, where potable water is made along with concentrated brine. Also, the NF brine has value as well – providing a stream rich in magnesium. The institution plans to use this to augment the SWRO permeate, which is used for drinking water. Many studies have shown the health benefit of increasing the Mg in desalinated potable water, which normally has very low values of Mg. (Cotruvo J and Bartram J)

The low-pressure NF system utilizes PRO XS-X membrane is a 2x1 array, with 6 vessels in the first stage, and 3 vessels in the second stage. Each stage has 6 elements per vessel. A unique membrane was developed for this trial, which has a very high magnesium rejection. The comparison of Mg, $SO_4$, and Cl for these various NF membranes is shown in Figure 6.

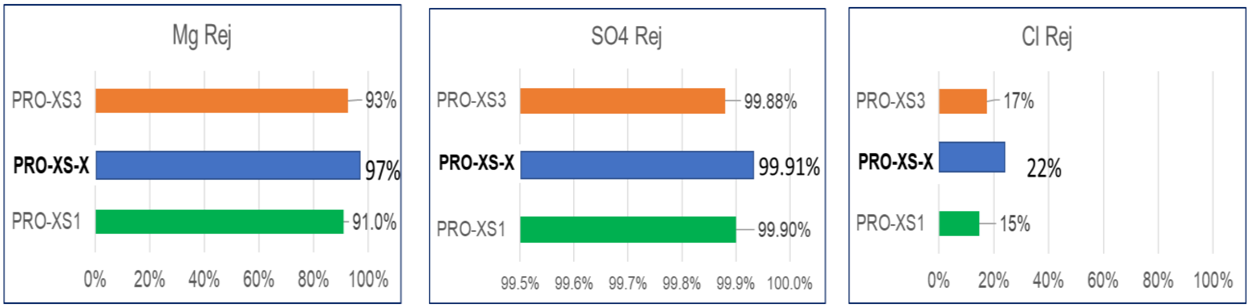


Figure 6. Select ion rejections for three NF membranes tested on synthetic seawater at 15 gfd flux and 15% recovery.

As seen in the data, the membranes have a unique ability to reject divalent ions, while passing the monovalent ions. For this type of water chemistry, it is possible to run at up to 80% recovery with antiscalant. Table 1 shows that the design values, which were quite close to the actual values of operation.

Table 1 Design and Actual operation parameters for low pressure NF pilot at Jubail.

| | **Projected** | **Actual** | **Rej (%)** |
|---|---|---|---|
| Feed Press (Bar) | 21.5 | 19.9 | |
| Feed Temperature, deg C | 29 | 29.1 | |
| Recovery (%) | 80% | 80.20% | |
| Perm Flow (m3/h) | 42.6 | 42.6 | |
| Brine Flow (m3/h) | 10.4 | 10.4 | |
| Stg 1 Brine Press (Bar) | 20.9 | 19.2 | |
| Stg 2 Brine Press (Bar) | 18.8 | 20.3 | |
| Perm Mg (mg/L) | 147 | 150 | 96.6 |
| Brine Mg (mg/L) | 7686 | 7200 | |
| Perm Cl (mg/L) | 19,240 | 19,881 | 33.6 |
| Brine Cl (mg/L) | 40,774 | 36,406 | |
| Perm SO4 (mg/L) | 2.0 | 2.0 | 99.98 |
| Brine SO4 (mg/L) | 17,141 | 19,500 | |

Initial pilot operating data for the low-pressure NF membranes is shown in Figure 7. A) Feed and permeate water conductivity trends. B) Stream flow rates and feed pressure.

As can be seen by the data, the permeate conductivity is not much different than the feed, since the membrane is passing most of the monovalent ions, and only rejecting divalent ions. The feed pressure increases slightly just at start-up but is then steady throughout the operation period. The stable flow and pressure indicate that there is no scaling on the membrane, as desired.

HIGH PRESSURE SWRO/UHP RO – Key design parameters for SWRO and UHP RO are given in Table 2. The first stage utilizes 8 pressure vessels, each with 6 SWRO elements (SWC5 LD), while the 2nd stage utilizes 2 pressure vessels, each with 6 UHP RO elements (PRO XP1). For such high feed salinity, a traditional single stage SWRO system may only run at 40-45% recovery, at which point it would reach the maximum feed pressure for the membranes. In this pilot, we have been able to operate at much higher recovery of 67%. This is a result of two new technologies, as previously mentioned. Firstly, the system utilizes new ultra-high-pressure RO membranes, which can operate up to 1740 psi (120 bar) at 30 C. In this application where the feedwater is above 30C, the maximum allowed feed pressure is slightly lowered. With a broader operating pressure allowance, the brine can be concentrated to 100-120k ppm TDS.

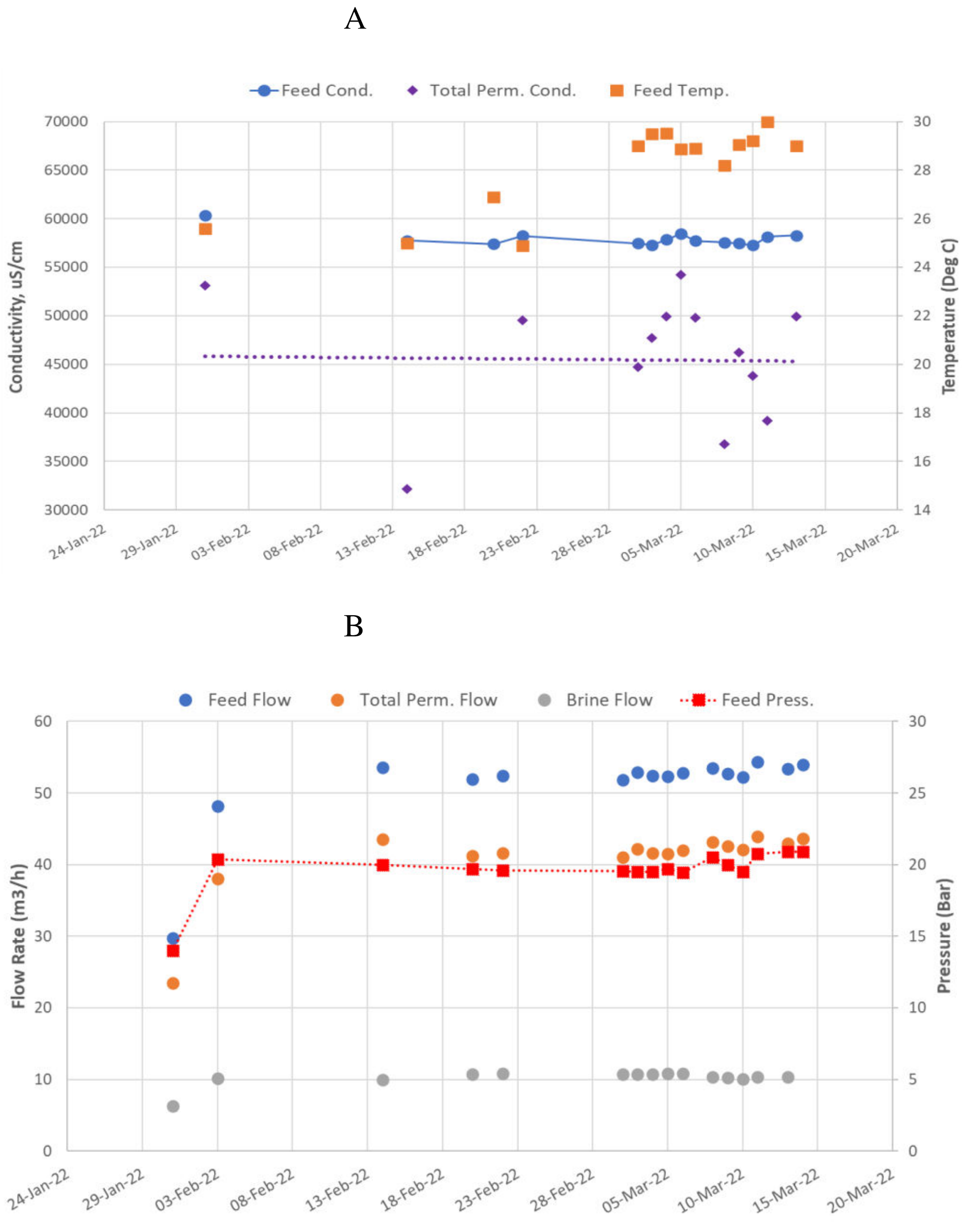


Figure 7. Performance trends for the low-pressure NF system

The second innovation is the utilization of two connected turbos employing the Turbocharger concept. These allow the feed pressure to each stage to be optimized to the desired flux. In our pilot, the pressure to the second stage UHP RO membranes is boosted to 608 psi (41.9 bar) to reach 1607 psi (110.8 bar). The exhaust from this 2nd stage turbo is still at 385 psi (26.5 bar), so it is used to drive the 1st stage turbo, which then provides a 64 psi (4.4 bar) boost. The pressure boost of each can be adjusted and tailored based on fouling, temperature, etc to achieve the desired stage 2 feed pressure and provide some added boost to the first stage.

Table 2 Design and operating data for the SWRO and UHP RO in the Jubail pilot.

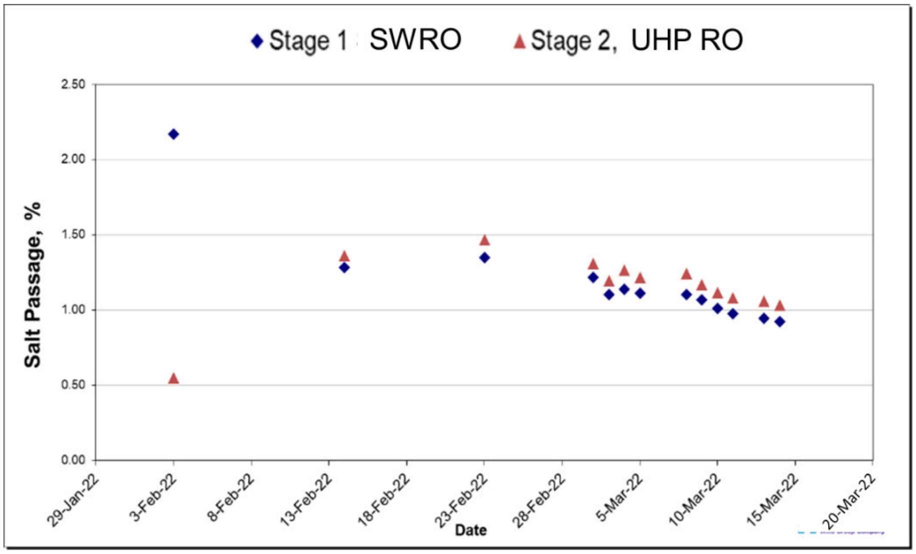
| | **Projected** | **Actual** | **Rej (%)** |
|---|---|---|---|
| HP Pump Press (Bar) | 54.9 | 60.1 | |
| Feed Press (Bar) | 60.6 | 64.6 | |
| Recovery (%) | 67% | 67% | |
| Perm Flow (m3/h) | 28.4 | 28.4 | |
| Stg 1 Brine Press (Bar) | 60.4 | 64.3 | |
| Stg 2 Brine Press (Bar) | 94.5 | 98.5 | |
| Stg 1 Boost Press (Bar) | 5.7 | 4.5 | |
| Stg 2 Boost Press (Bar) | 35.2 | 35.2 | |
| Stg 1 Exhst Press (Bar) | 1.0 | 0.2 | |
| Stg 2 Exhst Press (Bar) | 27.7 | 28.1 | |
| Brine Mg (mg/L) | 544 | 565 | 99.9 |
| Perm Cl (mg/L) | 267 | 431 | 98.9 |
| Brine Cl (mg/L) | 94,784 | 92,900 | |

The trend data for this two-stage system is shown in Figure 8. There is some change in the performance of the membranes, which is due to compaction that occurs at these extreme conditions. This improves the salt rejection (decreases salt passage) as seen in Figure 8A, but causes an increase in pressure and decrease of normalized flow as seen in Figure 8B. However, the effect is not significant. The key aspect is that the membrane performance is relatively stable and able to achieve a brine of 100-110k mg/l TDS which is comprised mostly of NaCl. This is the product from which the feedstock to the chlor alkali plant will be generated after further concentration. Figure 8B also shows the much higher pressure of the 2nd stage versus the 1st stage. This is the benefit of the turbo employed in the 2nd stage. This small turbo pump is extremely efficient and small. It fits easily into the system and operates smoothly and quietly.

The benefit of these two new technologies allows a simple system design, low capital expense and a low energy consumption. The low-pressure NF utilized 1.60 kWh/m3 of energy, while the

SWRO/UHP RO system had an energy consumption of 3.62 kWh/m$^3$, for a total of 5.22 kWh/m$^3$.

A



B

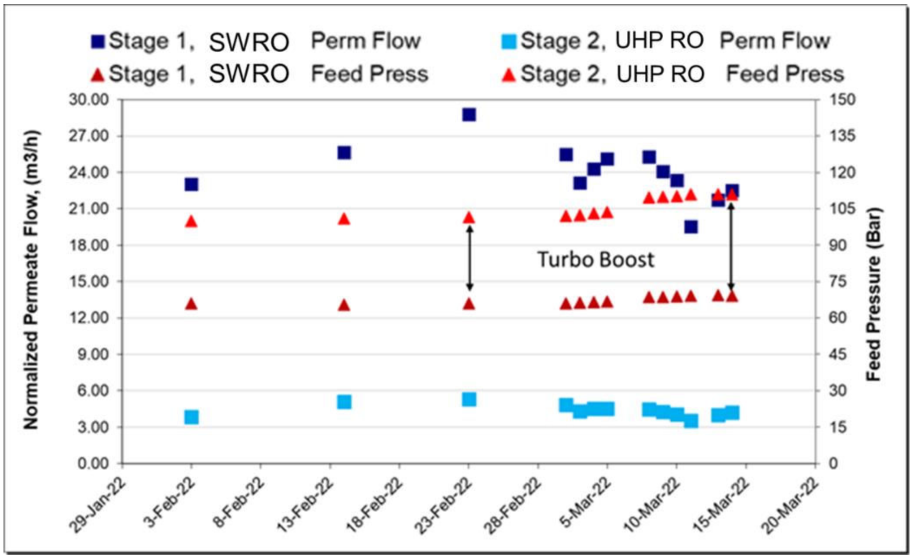


Figure 8 Operation trend data for the SWRO and UHP RO systems in the Jubail pilot. A) salt passage trend, B) Pressure and flow trends

HIGH PRESSURE BRINE CONCENTRATION – As is well known, RO first requires pressure to overcome the system osmotic pressure, at which point any additional pressure will cause water flux across the membrane. With high rejection membranes, the osmotic pressure is roughly the osmotic pressure of the feed/brine solution. For seawater membranes, the evolution of osmotic pressure can be typically shown in Figure 9, where the calculated feed and brine osmotic pressures are shown for each element in a seven-element vessel. The limiting factor is the osmotic pressure of the brine solution at the final recovery value. At this point, the feed pressure is only marginally greater than the osmotic pressure, providing little driving force to pass water through the membrane. Thus, as RO processes go to higher salinities, the osmotic pressure becomes so large it is impractical to run with traditional membranes.

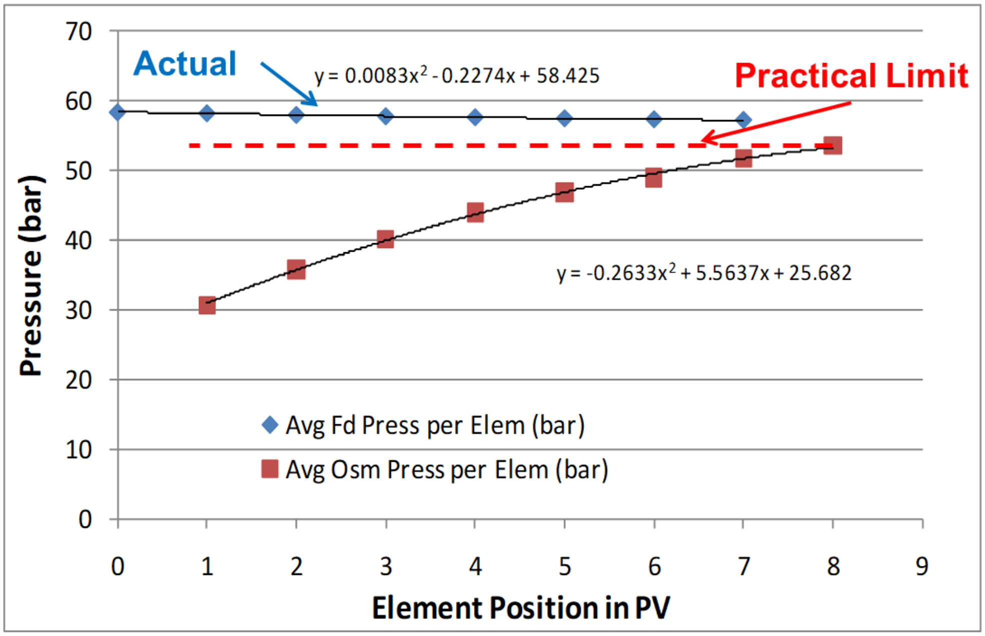


Figure 9 Simulation of the pressures in a SWRO 7 element pressure vessel in which feedwater is 39,000 mg/l TDS and 50% recovery.

Instead of making RO membranes more robust for 2000+ psi, there is a new trend to use lower rejection membranes, which will pass salts more readily, which in turn, reduces the osmotic pressure of the system. These are thus only used for concentrating the salt, since the permeate salinity would be too high for potable or most industrial use. When tested at traditional SWRO lab conditions (32,0000 mg/l NaCl and 600 psi), these membranes would have 85-95% rejection, well below the traditional 99.8% rejection of SWRO membranes. That puts these membranes in the category of nanofiltration or loose RO type membranes. Some people also refer to these as osmotically assisted RO (OARO). At the rejection values described above, it is possible to run these brine concentration membranes at pressures like traditional SWRO, 900-1100 psi.

Understanding the properties of these membranes and applying them to treat SWRO/UHP RO brine is now actively being investigated. One characteristic which is key to understanding their

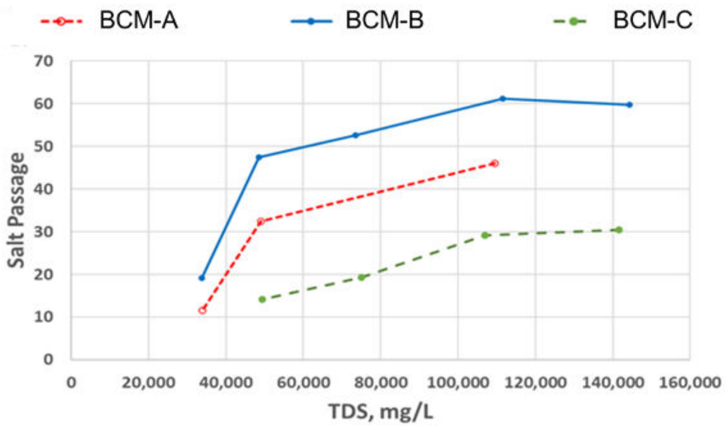


Figure 10  Salt passage performance of three brine concentration membranes as a function of feed salinity for a synthetic seawater feed stream.

application is salinity effects. Figure 10 shows the change in rejection as a function of the feed salinity. Three different brine concentration membranes (BCM) were tested, PRO XS A, B and C. These have salt rejections of 93, 88 and 96% at 32,000 mg/l NaCl and 600 psi. As the feed salinity rises, the salt passage of each membrane increases (lower rejection). The lowest rejection membrane, BCM-B, has the biggest salinity effect, while the highest rejection membrane BCM-C, has the smallest effect. This characteristic is due difference in the rejection mechanism of the two membranes. The looser membrane utilizes more of charge repulsion to achieve the salt rejection, while the tighter membrane uses more size exclusion. As the feed solution reaches higher strength, the charge interactions between the membrane and solution ions, become less impactful, while molecular sieving effects are less affected.

Analysis of various design options demonstrates that the higher brine solutions would need to be treated with the looser membranes to pass enough salt to keep osmotic pressure in the range of what we have for SWRO. The other key design feature being promoted by the institution is the use of recycling the highly saline permeate back to the previous stage for further recovery of the salts and product of pure water. As shown in Figure 3, the permeate from the first brine concentration stage is sent back as feed to the SWRO. It turns out that the permeate from this stage is nearly equal to the salinity of the feedwater to the SWRO. The SWRO will recover drinking water from this recycled water and concentrate the salts for further use. The second stage brine concentration permeate is fed back to the first stage brine concentration membranes. Again, the salinity of this permeate is similar to the feed salinity of the 1st stage, so it is well balanced. The penalty for this recycled permeate concept is the added power to repressurize the permeate and the larger system design required to handle the additional flow of the recycled permeate.

A conceptual design utilizing these brine concentration membranes is shown in Figure 11. In Figure 11A, the low-pressure NF concentrates the Mg to 7,200 mg/l and passes a permeate with 38,000 mg/l TDS. The permeate is treated with SWRO to reach 68,000 mg/l TDS, which is then treated with UHP RO in two stages to reach 126,000 mg/l TDS. The combined permeate from the SWRO/UHP RO is 750 mg/l TDS. In this case, the Turbocharger energy recovery devices are placed on the feed to the two UHP RO stages and provide all the pressure needed to run at the required flux. Only the main high-pressure pump to the SWRO is needed to generate ~950 psi (65 bar) of pressure.

For the brine concentration stages, the higher rejection BCM-A is used in the first stage, while the looser rejection BCM-B is used in the 2nd stage, where feed salinity is higher. Again, the higher passage of salts in this second stage is needed to keep osmotic pressure at similar ranges as in SWRO. In this example, the high-pressure pump would generate 855 psi (59 bar) of pressure, and the 1st stage turbo would add 220 psi (15 bar) of pressure, which is recovered from the exhaust of the 2nd stage turbo. The brine from the 1st stage will have a salinity of 173,000 mg/l TDS but due to the use of the lower rejection BCM-B, the feed pressure required for stage 2 is only 1015 psi (70 bar).

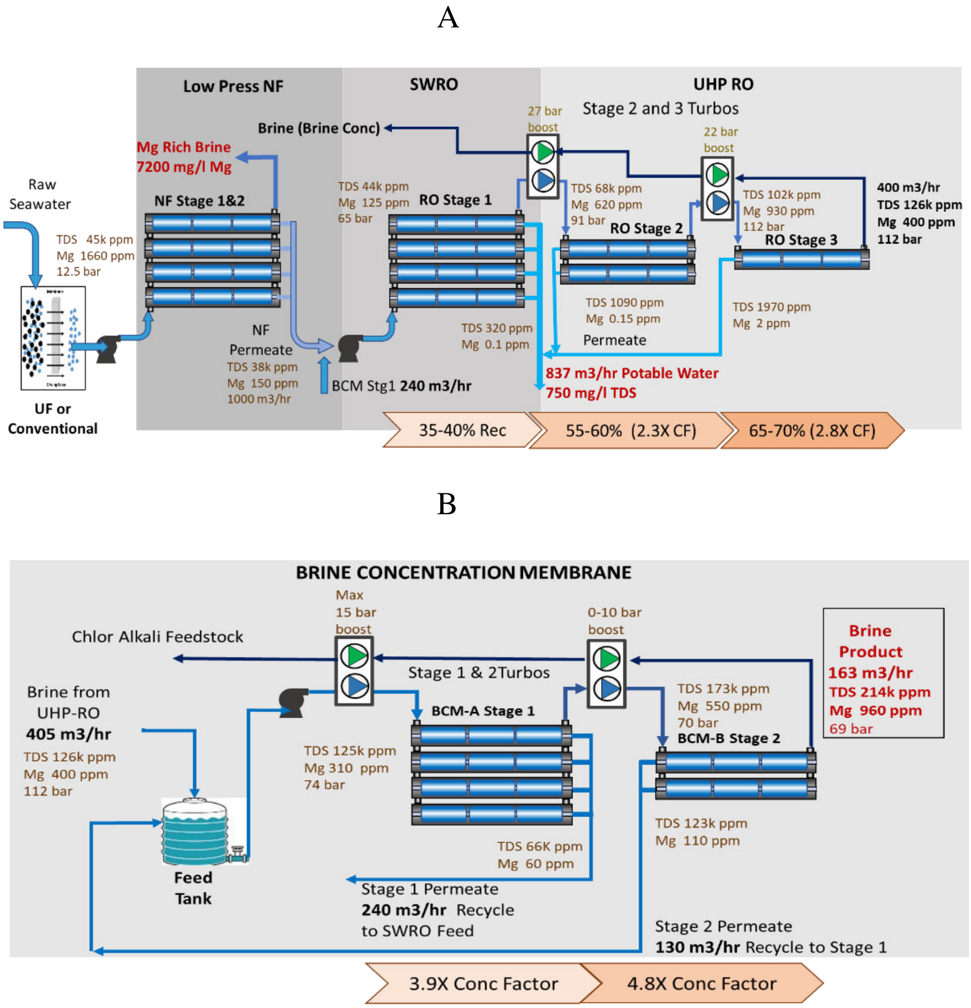


Figure 11 Conceptual design of ocean bine recovery system. A) The low pressure NF and high pressure SWRO/UHP RO system, and B) The Brine concentration membrane system.

The bine from stage 2 will have 214,000 mg//l TDS, and a small amount of this brine stream pressure would help drive the 2nd stage turbo (0-140 psi), while most would supply the first stage turbo. At this concentration or even higher values which can be achieved, the brine can go directly to crystallizers and avoid the use of expensive evaporators.

Testing of the brine concentration membranes is now underway in Jubail, and data will be generated to further refine these models and designs, but initial calculations indicates that the design concept of Figure 3 can be very energy efficient, making the recovery of valuable minerals from the ocean very economical. Based on the design in Figure 11, the specific energy demand would be 5.1 kWh/m$^3$ of RO permeate. According to financial estimates (Voutchkov 2022), brine from one 100,000 m3/d SWRO plant can produce up to 1.2 million dry tons of NaCl per year. In terms of revenue from these products (not including Mg), water would be sold at $0.60/m3 or $22 million per year, while the NaCl brine would be sold for $65 million/year. Thus, it can be seen that the brine would be the more valuable product. The institution along with its parent organization, Saline Water Conversion Corporation (SWCC), is planning to have a large-scale brine mining plant to recovery 1 – 2 million dry tons of NaCl by 2025.

## CONCLUSIONS

With the advent of new membranes and new energy recovery devices, it is possible to concentration seawater up to 214,000 mg/l or higher. This energy efficient process makes it possible to then recovery NaCl and Br from the brine at economical costs. Critical to this process use of low-pressure NF, SWRO, UHP RO and new brine concentration membranes. These four membrane types can work together in an energy efficient manner to generate useful Mg brine, NaCl+Br brine as well as valuable potable water. The piloting of these processes has shown good agreement with design values and the capability to run stably at these conditions. Not only will this make ocean brine mining a viable industry, but these processes can also be applied to many industrial wastes or brine well waters to achieve recovery of valuable minerals or reduction in the waste liquid to achieve minimum liquid discharge (MLD) or zero liquid discharge (ZLD). System designers will need to work closely with the membrane and pump companies to design efficient systems for the application of this new technology.

# REFERENCES

Saltworks, (2018). What is Zero Liquid Discharge and Why is it Important. On-line Article *https://www.saltworkstech.com/wp-content/uploads/2018/04*

Voutchkov, N. (2022). Overview of DTRI System for Brine Mining of NaCl and Br. *Proceedings of Ocean Brine Mining Workshop, Jubail, KSA 2022.*

Cotruvo J, Bartram J, eds. (2009). Calcium and Magnesium in Drinking-water: Public Health Significance, World Health Organization Press, Switzerland.