Membrane Brine Concentration for NaCl Salt Production from Seawater

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Abstract

The recent development of osmotically-assisted reverse osmosis (OARO) has opened new opportunities for employing membranes in high salinity applications traditionally only served with thermal techniques. By decoupling feed pressure and osmotic pressure, brine concentrations of over 250 g/l can be achieved at modest operating pressures. However, high concentration factors pose the risk of the precipitation of sparingly soluble salts (scaling) on membrane surfaces. While such species can be reduced or removed by physiochemical separation techniques such as precipitation/clarification, the associated chemical consumption rates may be cost- and logistically-prohibitive. Also, it can be challenging to combine a high-pressure membrane process with a precipitation process from an operational standpoint. Nanofiltration (NF), where membranes reject divalent ions at higher rates than monovalent ions, could nominally be combined with OARO to provide an all-membrane solution for high concentration factors. However, for ZLD applications, the NF reject can be as cumbersome and costly to dispose of as the liquid discharge the overall process is designed to minimize. For brine mining applications, NF membrane selectivity may be inadequate for meeting mineral quality requirements.

Sodium chloride (NaCl) salt production from seawater is one application where NF and OARO can be combined advantageously with reduced downsides. When brine discharge to the sea is not constrained, NF reject can be inexpensively disposed of. Moreover, if NaCl purity of over 97% can be achieved in the NF permeate, an OARO process can be applied to concentrate it with very little reduction in purity and with minimal risk of membrane scaling.

This paper presents design considerations and performance and cost analyses for a proposed process using NF, seawater reverse osmosis (SWRO), OARO and thermal unit operations to produce NaCl salt from seawater. Commercially available NF membranes are compared to assess key performance characteristics. Important design characteristics for OARO are considered. In addition, the study includes quantified estimates of operating and capital costs for alternative process configurations.

Introduction

Of the many dissolved constituents of seawater, sodium chloride is the most abundant, comprising over 86% of the total dissolved solids [Lenntech (2023)]. Among its many uses, sodium chloride is feedstock for the chlor-alkali industry. Although the primary source of sodium chloride for the chlor alkali industry are mines [ITP (2023)], its production from seawater is potentially more sustainable given the abundance of seawater. Concurrently, there is new interest in mineral production in the context of minimum- or zero-liquid-discharge seawater desalination as a means to produce valuable resources while reducing the impacts of desalination brine discharge to the environment [NEOM (2023)]. In addition to sodium chloride, magnesium, calcium sulfate and potassium are also abundant and valuable constituents of seawater.

The development of osmotically-assisted reverse osmosis (OARO) has opened new opportunities for employing membranes in high salinity applications traditionally served with thermal techniques [Stover, Choong, Govindan, (2018); Stover, Lokare (2020); Stover, Lokare (2022)]. In addition, nanofiltration (NF), which rejects divalent ions at higher rates than monovalent ions, can be combined with OARO to provide an all-membrane method for mineral refining and concentration.

Concentration of Seawater

Reverse osmosis (RO) is widely applied to desalination and saline water treatment applications in part because of its proven reliability, relatively low capital cost and low energy requirements compared to traditional thermal techniques. However, seawater reverse osmosis (SWRO) is limited to 1,200 psi (83 bar) and about 96,000 mg/l total dissolved solids (TDS) by the high osmotic pressure of concentrated salt solutions. Figure 1 illustrates the osmotic pressure of several salts over concentration ranges of interest for desalination and mineral production applications. Osmotic pressure increases sharply with concentration.

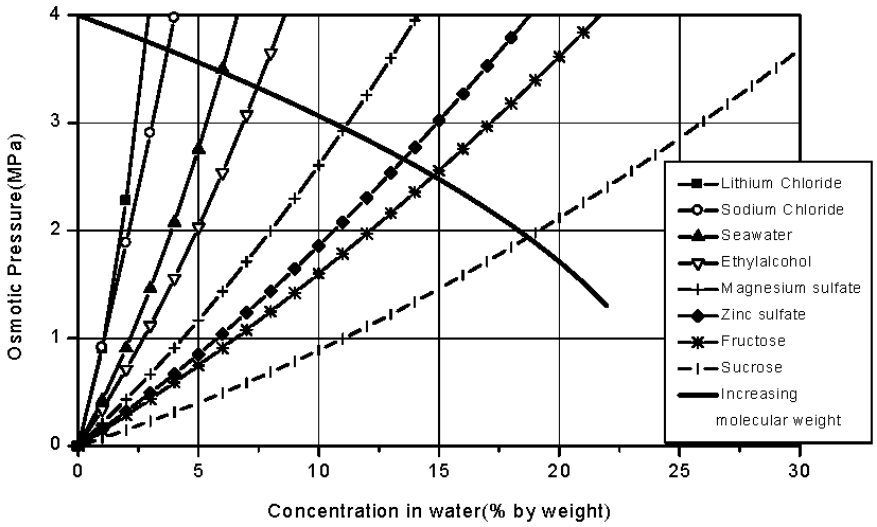


Figure 1. Osmotic Pressure of Salt Solutions as a Function of Concentration [Toray (2009)]

Disc tube RO and ultra-high-pressure RO (UHPRO) can be operated at pressures of up to 1,800 psi

(124 bar), increasing brine concentrations to as high as 130,000 mg/l TDS. However, such high-pressure operation presents potentially prohibitive challenges for equipment sourcing, in addition to possible worker safety concerns. Perhaps more importantly, membrane brine concentrations of over 200,000 mg/l TDS are desired to minimize the size of downstream thermal crystallization operations, as discussed in subsequent sections of this paper, and such concentrations are not feasible with available UHPRO equipment.

In addition to pressure requirements, high brine concentrations in membrane systems poses potential risk of the precipitation of sparingly soluble salts, or scaling, on membrane surfaces. However, the high ionic strength of seawater keeps most salts in solution to high concentrations. Figure 2 is an antiscalant projection which shows that up to 69% recovery or 114 g/l total dissolved solids (TDS) is feasible from standard seawater, even without antiscalant dosing (red bars). Sulfate salts and calcium fluoride are the primary scaling species of concern. Rejection of sulfates and hardness by NF membranes essentially eliminates scaling risk in a downstream high-recovery SWRO process on NF permeate.

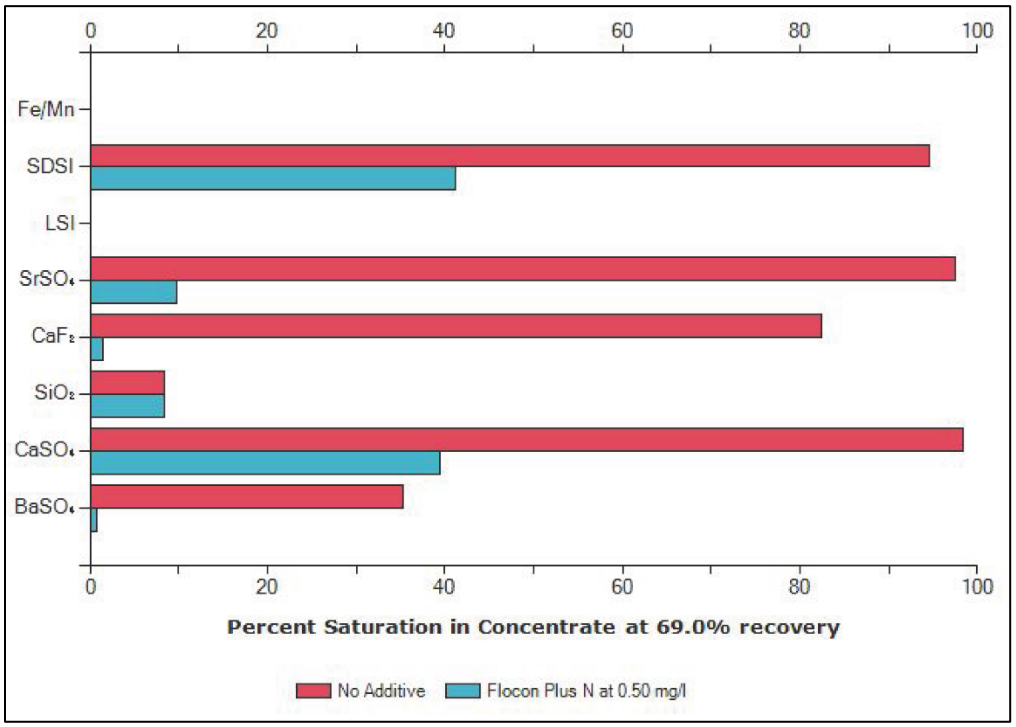


Figure 2. Sparingly Soluble Salt Concentrations at 69% Recovery with SWRO Membranes [BWA (2023)]

Membrane Brine Concentration

The proposed scheme for treating seawater to produce sodium chloride is illustrated in the following simple process flow diagram.

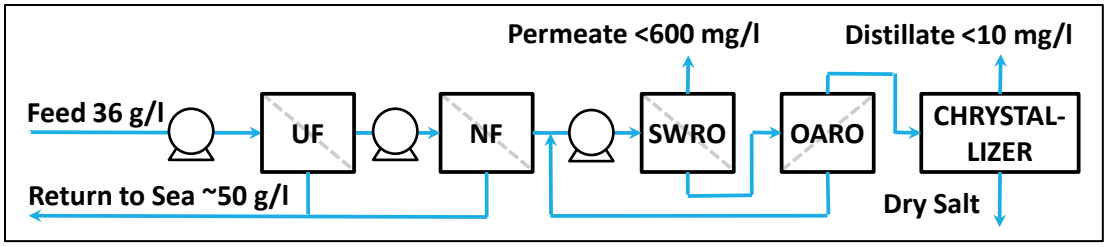


Figure 3. Process Flow Diagram of Proposed Sodium Chloride Production Process

The unit operations within the process are discussed in the sections below.

Pretreatment

Screened seawater is pretreated with ultrafiltration at approximately 95% recovery. UF backwash and chemically enhanced backwash are blended with NF reject and returned to the sea.

Nanofiltration

Nanofiltration (NF) is applied to the UF effluent to reject divalent ions, producing monovalent-rich permeate for downstream concentration. It should be noted, however, that the selectivity of NF processes can vary significantly as a function of membrane type and recovery rate. The following table illustrates selectivity performance for two commercial NF models operated at 75%. Ideal performance for the proposed process includes maximum NaCl purity in the permeate and minimum reject TDS. Based on these criteria, NF type A is best suited for this application.

Table 1. Selectivity Performance of Two Commercial NF Types [Veolia (2023); Dupont (2022)]

	NF A			NF B		
	feed	reject	permeate	feed	reject	permeate
NaCl purity	86%	68%	98.2%	86%	77%	94.7%
Ca, mg/l	410	1,299	113	410	1,076	188
Mg, mg/l	1,310	4,962	91	1,310	3,567	558
TDS, g/l	35.8	56.2	28.7	35.8	71.5	23.9

Projections were also run with both NF membrane models at 90% recovery. Although both membranes are nominally capable of operating at 90% recovery without exceeding their pressure ratings, selectivity is reduced, resulting in higher permeate TDS and lower NaCl purity than at 75% recovery. Projections were also run at pH 5 with sulfuric acid dosing to test the theory that excess sulfate could increase calcium rejection and thereby increase NaCl purity in the permeate. However, seawater contains an abundance of sulfate such that additional sulfate has negligible benefit.

For typical RO applications, it is possible to enter the feedwater composition into an antiscalant projection program, select the membrane type and desired recovery rate and get a reasonably accurate prediction of brine composition. However, because NF selectivity can vary significantly as illustrated above, it is advisable to enter the NF brine composition from the membrane projection into the antiscalant projection program and compute scaling potential at zero recovery rate. Such analyses, conducted for both membrane types presented in Table 1 above, showed that at 90% recovery, brine from NF type A had significant scaling potential whereas brine from NF type B did not, consistent with the higher divalent rejection performance of type NF type A. Brine produced

at 75% recovery did not have significant scaling potential with either membrane.

In considering application of NF for divalent rejection in minimum- or zero-liquid discharge (MLD, ZLD) applications, it should be noted that NF reject can be as cumbersome and costly to dispose of as the liquid discharge the overall process is designed to minimize. However, for NaCl production from seawater, NF reject can typically be disposed of to the source. In the proposed process, NF reject is blended with UF backwash for disposal. The combined salinity is approximately 50 g/l TDS.

Osmotically-Assisted RO

As explained above, the osmotic pressure of saline solutions increases sharply with concentration. RO feed pressure increases accordingly. However, if the permeate is saline, feed pressure is reduced in proportion to the difference between the osmotic pressure of the feed/brine and the permeate. This is the phenomena exploited by OARO technology to enable the production of ultra-high brine concentrations at relatively low feed pressures.

There are two general means to apply salinity to the permeate side of membranes. One is directly, using hollow fiber membranes. This was the approach originally proposed by Syd Loeb in a British Patent [Loeb (1971)], from which the below figure was extracted.

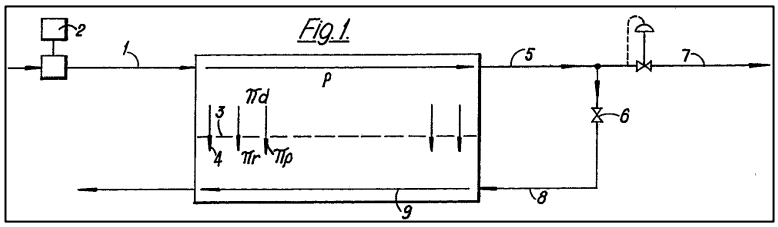


Figure 4. Illustration from Sydney Loeb Patent [Loeb (1971)]

An expanded process scheme with hollow fiber membranes is given in the figure below. Multiple stages are arranged in series. Higher concentration factors require more stages. Feed/brine concentrates across the top of the diagram from left to right. Final brine is depressurized through an energy recovery device (ERD) or a throttle valve. A portion of the final brine is applied to the permeate side of the last stage. Permeate pumps are required because the pressure drop through the fiber lumens is relatively high. One permeate pump is required per stage to minimize permeate side pressure. Permeate dilutes as it cascades from right to left in the diagram. OARO stage 1 in the diagram is a conventional RO stage, fed with a blend of raw feed and dilute OARO permeate, producing RO-quality permeate.

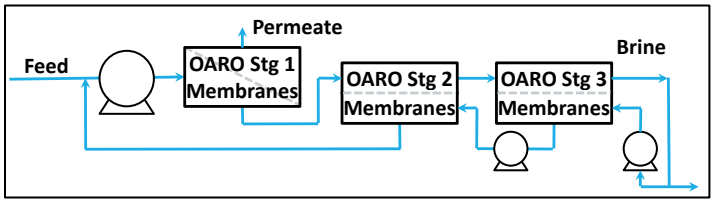


Figure 5. Process Diagram for OARO with Hollow Fiber Membranes

The other commonly applied means to apply salinity to the permeate side of membranes makes use of RO membranes with very high salt passage in spiral format [Herron, Beaudry, Lampi (2015); Wang, Deshmukh, Du, Elimelech (2020)]. This process is also deployed in multiple stages, with more stages required to achieve higher concentration factors. However, OARO staging differs from conventional multi-stage RO staging, as illustrated in the figures below.

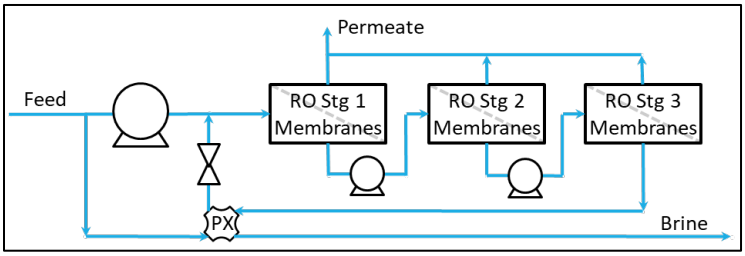


Figure 6. Traditional Multi-Stage RO Process with Interstage Boosting

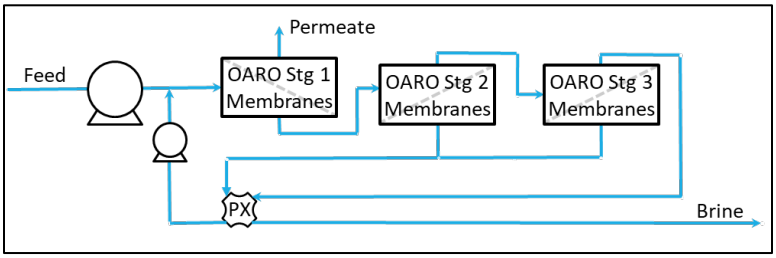


Figure 7. Process Diagram for OARO with Spiral Membranes

In a traditional multi-stage RO process of Figure 6, interstage pumps boost pressure to overcome the increasing osmotic pressure of the concentrating feed/brine stream. This approach is limited by the maximum pressure rating of RO membranes and equipment. In addition, interstage pumps add to capital expense. Also, if high-efficiency isobaric-energy-recovery is to be employed to minimize energy consumption, pressure must be throttled through a valve upstream or downstream of the ERD for return to the process, reducing energy savings. Alternately, a less energy-efficient turbine-type ERD must be used in series with a larger high pressure pump [Stover (2022)].

In the OARO process illustrated in Figure 7, feed pressure is not typically boosted between stages. Indeed, pressure decreases slightly through each successive stage because of hydraulic resistance through the feed/brine channels, commonly known as differential pressure drop. Therefore, OARO membranes with higher water permeability and lower salt retention are selected for later stages fed with higher salinity. The concept of ideal salt retention is illustrated in the following figure.

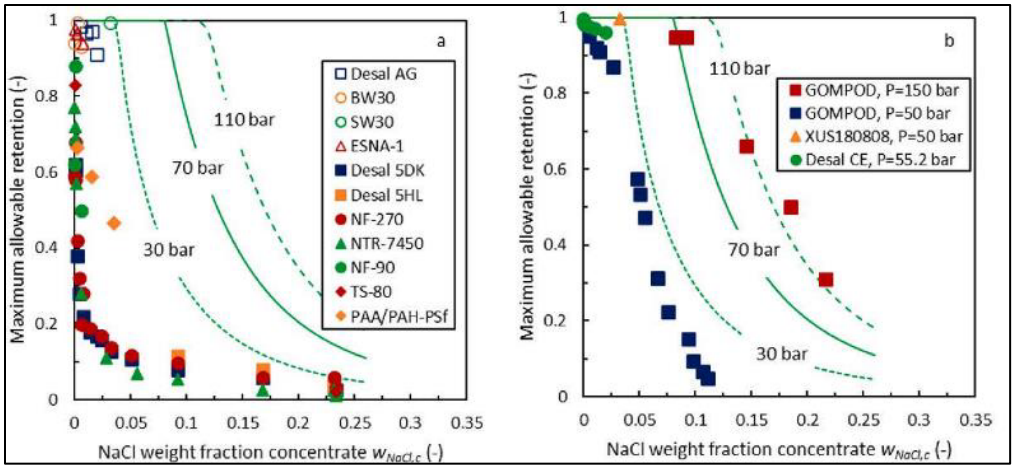


Figure 8. Ideal Salt Retention as a Function of Feed Salinity [Bargeman (2023)]

In Figure 8, ideal salt retention at different pressures is shown as green lines, with a typical operating pressure being 70-80 bar (1,000-1,160 psi). Tested performance of a few commercially available RO and NF membranes are arranged in the figure on the left. The large distance between the retention of these membranes and the green lines clearly illustrates that these membranes are incapable of providing ideal salt retention over the salinity range of interest. The figure on the right shows that the performance of two experimental membranes much more closely approaches ideal retention. New membranes that exhibit ideal or close to ideal performance are being produced and tested by major membrane manufacturers [Bartels, Huang, Franks (2023)].

Returning to the OARO process flow diagram in Figure 7, membranes with reduced salt retention or higher salt permeance are arranged in the OARO stages, with lower retention membranes applied in higher concentration stages [Lokare, Stover (2022)]. This concept is similar to internal staging or hybrid designs commonly used in RO systems since introduction of the concept in 2005 [Mickols, Busch, Maeda, Tonner, (2005)]. Proper arrangement of membrane types in an OARO system forms a permeance ramp that balances flux along the array, maximizing concentration per stage while minimizing the amount of salty permeate recycled in the process.

Returning to the overall process flow diagram in Figure 3 above, the SWRO unit receives softened seawater from the NF unit. SWRO brine cascades to the OARO unit which produces concentrated brine for feed to the crystallizer and salty permeate for return to the SWRO unit. A single high pressure pump drives feed/brine through the SWRO and OARO units. Permeate from the first several OARO stages is directed to the suction of the high-pressure pump. Saltier permeate from later OARO stages is recycled in the OARO stages, with smaller high-pressure pumps used to meet the feed pressure at the desired injection points. Recovery rates in the combined SWRO-OARO units can exceed 90% from NF permeate, producing a final brine with a concentration as high as 250 g/l or higher, approaching saturation.

Crystallizer

Referring again to Figure 3 above, a crystallizer receives OARO brine and produces dry salt and distillate. For this assessment, distillate recovery rate in the crystallizer is assumed to be 75% and distillate quality less than 10 mg/l TDS. For the process without OARO, the crystallizer receives SWRO brine and operates at 91% recovery. The specific energy consumption of the crystallizer was estimated to be 80 kWh/m^3 (303 kWh/1000 gallons) of feed [Leonescu (2020)]. The capital cost, energy consumption and other requirements of crystallizers are considered below and shown to be much higher than for OARO on a per-unit-of-water-treated basis. Therefore, a goal of the proposed process is to maximize concentration through the membrane stages to reduce flow to the crystallizer.

Performance and Cost Modelling

Stream compositions for the proposed process are listed in the table below. The data indicate very high purity NaCl in the NF permeate, and this purity is substantially maintained through the SWRO and OARO units because very little salt is lost in the SWRO permeate.

Table 2. Proposed System Stream Compositions

	raw feed	NF reject	NF permeate	SWRO + OARO brine	SWRO permeate	Crystallizer distillate
Na	10,982	11,498	10,809	93,994	225	
Cl	19,700	26,706	17,361	151,016	355	
Ca	410	1,299	113	1,001	0	
Mg	1,310	4,962	91	808	0	
K	390	438	374	3,239	10	
SO4	2,745	10,939	11	100	0	
Br	65	68	64	547	3	
TDS	35,776	56,167	28,697	251,189	597	10
NaCl purity	85.8%		98.2%	97.5%		

A cost analysis was conducted of the for the system depicted in Figure 3, sized for the flow rates in the following table. The NF unit was comprised of three stages, with permeate throttling to balance flux. The SWRO unit was comprised of two stages, with a combination of internal staging and permeate throttling to balance flux. The OARO unit consisted of six stages. The SWRO unit was fed with NF permeate and, when operated with OARO, salty permeate from the last four OARO stages. Without OARO, the SWRO unit was fed only NF permeate.

Table 3. Flow Rates for Capital and Operating Costs Analysis

Assumptions	with OARO	no OARO
UF feed flow, m^3/d	8,421	8,421
NF feed flow, m^3/d	8,000	8,000
SWRO feed flow, m^3/d	8,552	6,000
Crystallizer feed flow, m^3/d	684	1,807
Crystallizer feed TDS, g/l	251	95

Permeate flow, m^3/d	5,836	5,836
NaCl, ton/d	62,092	62,092

Estimated specific costs for the alternative processes are presented in the following table on a per-ton-salt basis. Capital costs (CAPEX) include process equipment, framing, piping, process construction materials and labor, engineering and freight. Capital costs do not include civil works, intake, outfall or legal fees. Capital costs were amortized over 20 years at an interest rate of 6%. Operating costs (OPEX) include power at $0.10/kWh, chemicals, replacement membranes and spare parts. Operating costs do not include labor. For reference, the market price for NaCl in the USA is about $130/ton [Statista (2023)].

Table 4. Capital and Operating Costs for Proposed Process, With and Without OARO

$/ton NaCl	with OARO		no OARO	
	CAPEX	OPEX	CAPEX	OPEX
UF	$ 2.30	$ 5.08	$ 2.31	$ 5.29
NF	$ 2.71	$ 4.51	$ 2.70	$ 4.63
SWRO+OARO	$ 8.78	$ 23.48	$ 3.84	$ 13.64
Crystallizer	$ 10.68	$ 35.39	$ 19.16	$ 92.45
TOTAL	$ 24.47	$ 68.47	$ 28.00	$ 116.01
		$ 92.94		**$ 144.01**

Comparing costs with and without OARO, the increased size of the crystallizer without OARO significantly increases overall salt production costs, exceeding the market price for salt sale.

Summary and Conclusions

This paper presented performance and cost modeling for NF, SWRO and OARO processes applied to NaCl salt production from seawater. It was demonstrated that different NF membrane types provide very different selectivity for monovalent and divalent ions, with over 98% pure NaCl feasible. The concept of a permeance ramp in OARO staging was introduced as a means to balance flux and maximize concentration per stage while minimizing the amount of salty permeate recycled in the process. The use of OARO for concentration of NF permeate from seawater can achieve up to 90% recovery corresponding to 250 g/l TDS, suitable for feed directly to a thermal crystallizer. The application of OARO reduces the size of the crystallizer, significantly improving the economics of NaCl production.

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