Achieving Minimal Liquid Discharge (MLD) with Advanced Membrane Systems at Maximized Volume Reduction: 5X, 20X, 40X, and 70X!

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ABSTRACT

This paper presents brine management results and economics for water plant designers. Readers will learn how to concentrate brines to 130,000 mg/L total dissolved solids (TDS) with reverse osmosis membrane technology while avoiding scaling and fouling. The work is intended to inform widening use of membrane-based brine concentration systems in order to offset more expensive evaporation or disposal methods. Pilot test results are presented for cooling tower blowdown brine at 1,800 mg/L TDS. The pilot test consisted of ways to achieve multiple volume reduction factors (recovery): 5X (80%), 10X (90%), 20X (95%), 40X (97.5%), and 70X (99%). Each jump in volume reduction adds plant complexity and cost. Each step will be explained and mapped so readers can learn about the technology and investment required to take the next step in recovery improvements. Two new technologies were trialed and will be reviewed. First, a robotized chemical softening system designed for use with variable water chemistry. This system includes a real time calcium sensor and precipitation management system. Results from new ultra high-pressure reverse osmosis spiral wound membranes rated for 1,800 psi (120 bar) will also be disclosed.

INTRODUCTION

Reverse osmosis (RO) is the world's most dominant desalination technology. Although it is widely applied to potable water applications such as seawater desalination, it has gained interest for brine concentration applications over the last few years. This opportunity is accelerating with the advent of incremental technology improvements to both RO membranes and systems.

The authors, who build industrial thermally driven evaporators and crystallizers, observed that industrial water plant designers could benefit from up-to-date knowledge on brine concentration with lower cost membrane systems. New technologies are emerging that push the recovery of RO enabling a reduction in the size of much costlier downstream thermal systems.

The first group of RO technology include a series of operational actions that disrupt concentration polarization gradients at the membrane surface, frequently flush the system, and / or employ aggressive anti-scalants with saturation relief and recycle. This paper will not cover these methods since they are widely explored by others (Preston, 2018; Greenwood et al., 2017). This paper assumes that the feed solution is already saturated with scaling ions from an upstream RO employing the above-mentioned recovery pushing actions. The objective is to further concentrate the saturated solution with a RO membrane system by removing the fouling and scaling compounds to the correct level while employing new RO technology that enables extremely high brine concentration capability.

The paper presents these technologies in reference to a pilot case study on cooling tower blowdown covering multiple volume reduction factors (recovery): 5X (80%), 10X (90%), 20X (95%), 40X (97.5%), and 70X (99%). The incremental process steps and costs required to achieve each is explored. Volume reduction factors are presented as the primary metric - small recovery changes can be misleading. For example, boosting recovery from 95% to 97.5% may seem like gaining "only 2.5%"; however, this gain represents halving the brine volume. This means 50% less trucks sent to disposal or a 50% smaller evaporation pond or a 50% smaller downstream evaporator. The savings to a project or operator can be enormous.

REVERSE OSMOSIS ADVANCEMENT

Most industrial ROs face brine volume reduction limits related to one of three criteria: (1) scaling; (2) organics; or (3) osmotic pressure. Any one of these limits can retard the recovery and brine volume reduction potential of the RO or damage the membrane. In this paper we will explore how to remove or manage the first two limits – scaling and organic fouling – in order to reach the third ultimate limit: osmotic pressure.

For many years' spiral wound RO membranes had a maximum operating pressure of 1200 psi (80 bar), enabling aqueous sodium chloride concentration to a maximum practical limit of 80,000 mg/L TDS. With the advent of ultra high-pressure spiral wound reverse osmosis membranes (UHP-RO) rated for 1800 psi (120 bar), the osmotic pressure limit has increased by 50%, enabling an almost 50% reduction in brine volume if scaling and organic issues can be mitigated. Some readers may note that disk tube RO (DTRO) has achieved 1800 psi (120 bar) pressures for some time, albeit in a specialized system with unique vessels and flow passages. This work focuses on mass produced spiral wound RO membranes and not DTRO. Spiral wound represents the vast majority market share, availability, and ultimately lower cost due to their higher production volume.

A test was completed to determine the UHP-RO flux vs total dissolved solids for sodium chloride on a UHP-RO spiral wound 4” x 40” membrane element. The results are summarized in Figure 1 and shows that 120 bar (1800 psi) spiral wound RO membranes can concentrate sodium chloride to 130,000 mg/L, noting that another test completed for sodium sulfate reached 150,000 mg/L. Lower pressure 80 bar (1200 psi) membranes can only achieve 80,000 mg/L sodium chloride concentration.

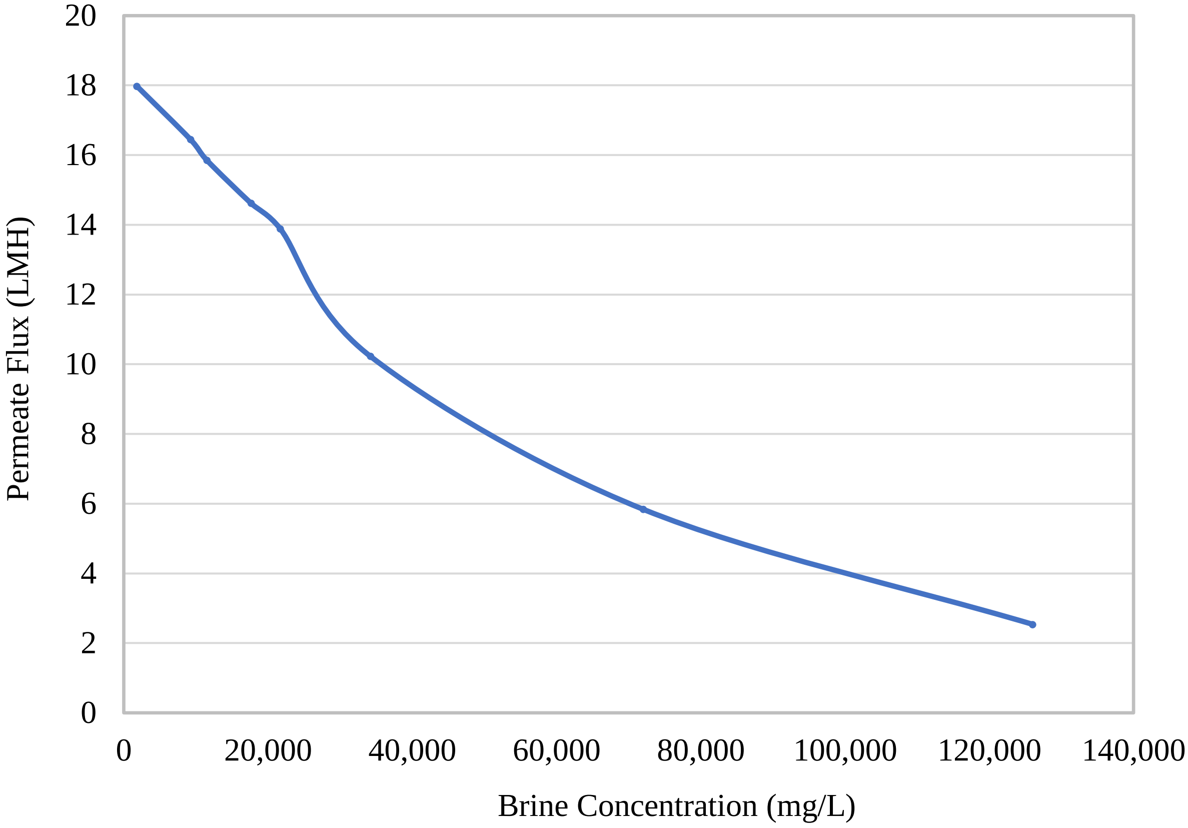


Figure 1: Ultra High-Pressure RO Flux with Sodium Chloride

At UHP-RO brine concentrations shown in Figure 1, the membrane permeate flux declines below the practical limit of 5-10 LMH (litres per m2 per hour) at the maximum brine concentration, which means more membranes, vessels, energy, and higher capacity hydraulic systems. However, even at fluxes of 5-10 LMH, RO is still more cost competitive than thermal systems and some disposal options. Reverse osmosis at 5-10 LMH may cost roughly $4/m3, inclusive of capital and operating cost but excluding at site permitting or civil works. In comparison to evaporators’ >$25/m3 costs or when disposal is > $5/m3, UHP-RO can add value.

In addition to the low permeate flux, UHP-RO permeate conductivity or total dissolved solids (TDS) is higher than traditional lower pressure ROs. One needs to keep in mind that semi-permeable membranes are specified based on percent salt rejection. Therefore, it is logical that higher brine concentration next to the membrane surface translates into increased permeate conductivity or TDS. Since UHP-RO may be part of a larger system with a lower pressure RO, opportunities may exist to blend the higher TDS UHP-RO permeate with other permeates to reach a discharge limit or use the UHP-RO permeate to flush upstream ROs. UHP-RO could be viewed as a brine concentrator and not necessarily a freshwater maker.

The above presented osmotic pressure limited brine concentrations could rarely, if never, be achieved on real industrial waters. Scale or organic fouling will hurt performance and/or damage the membrane before reaching these limits. It is therefore important to understand techniques to remove scale-causing ions and fouling-causing organics, which will accumulate at increased recoveries.

SCALE & ORGANICS MANAGEMENT IN REVERSE OSMOSIS

After having employed conventional RO to the maximum extent, more advanced scale or organic management techniques may be needed. However, to first push RO to its maximum extent one can apply strategies such as:

- Aggressive anti-scalants
- Monitoring membrane flux to sense degradation and take corrective action before it becomes irreversible
- Frequent and automated flushes, including high pH flushes for organics
- Semi-closed circuits with brine recirculation and concentration polarization disruption

In the cooling tower blowdown pilot disclosed herein, a primary RO was employed with some of the above techniques in order to achieve 5X volume reduction or 80% recovery. The primary RO (RO-I) brine emerged super saturated in silica ($SiO2$). At this point, scaling ion removal is required.

A well-known solution to remove scalants is chemical softening. This usually involves intensive use of chemicals, producing additional solid sludge waste and increasing operating costs. A combination of high pH and occasionally soda ash softening can effectively reduce scale causing compounds, such as silica, heavy metals, fluorides and calcium (sometimes magnesium needs to be added for silica precipitation). Table 1 lists the major scaling ions as well as the pre-treatment solution for each scalant.

Table 1: List of Typical Scaling Ions and Suggested Treatment Solutions

Scaling Ion	Pretreatment Solution	Concentration (Post Softening)
Si	pH 11 + Magnesium if not sufficiently present	< 5 mg/L
Mg	pH 11 (not a critical scalant, but will increase base consumption)	10-300 mg/L (heavily dependent on Mg levels)
Al	pH 11	case specific
Ca	pH 9-11 + Soda Ash	20 – 80 mg/L
Ba	pH 9-11 + Soda Ash	< 1 mg/L (depends on initial Ba levels)
Sr	pH 9-11 + Soda Ash	< 5 mg/L (depends on initial Sr levels)
Mn and Fe	pH 9-11 / oxidation / greensand	
F	pH 9-11	fluoride precipitates out
CO3	pH 5	

Traditional chemical softening was developed largely for municipal or mine water treatment systems without a membrane system downstream. It involves adding the chemicals in a system of one or two reactor tanks, dosing coagulants, and then settling out the precipitated scaling ion biproducts in a large clarifier, with an underflow filter press removing the solids.

However, chemical softening is not without its challenges, especially on variable and changing flows. These challenges include: (1) overdosing or underdosing chemicals; (2) space and sensitivity of clarification processes; and (3) sludge management. Overdosing will waste chemicals and increase solids load / TDS resulting in increased downstream processing costs or reduced flux of downstream membrane systems. Underdosing can cause scaling in the downstream assets. Another downside from chemical softening is the sludge / solids management. It can often require a very large surface area for the clarifiers due to gravity settling even with laminar clarifiers. Coagulants, such as ferric chloride, are often added for coagulation to help form larger particles which will settle faster. However, coagulants can leave iron or aluminium remnants that foul downstream ROs. Large scale RO plants in China's coal-to-chemicals industry have suffered notably by applying the traditional chemical softening technique, experiencing rapid membrane fouling resulting in frequent chemical cleans. The root cause often being the coagulation step and excess iron or aluminum that enters the downstream RO and fouls the membranes.

The authors have developed a different approach to chemical softening, leveraging the same known chemistries while aiming to remove the challenges disclosed. This is an advanced chemical softening technology, called BrineRefine, (Saltworks Technologies Inc., 2018) that produces a RO friendly discharge, with reduced scaling potential, as well as precipitated solids in a filter cake form.

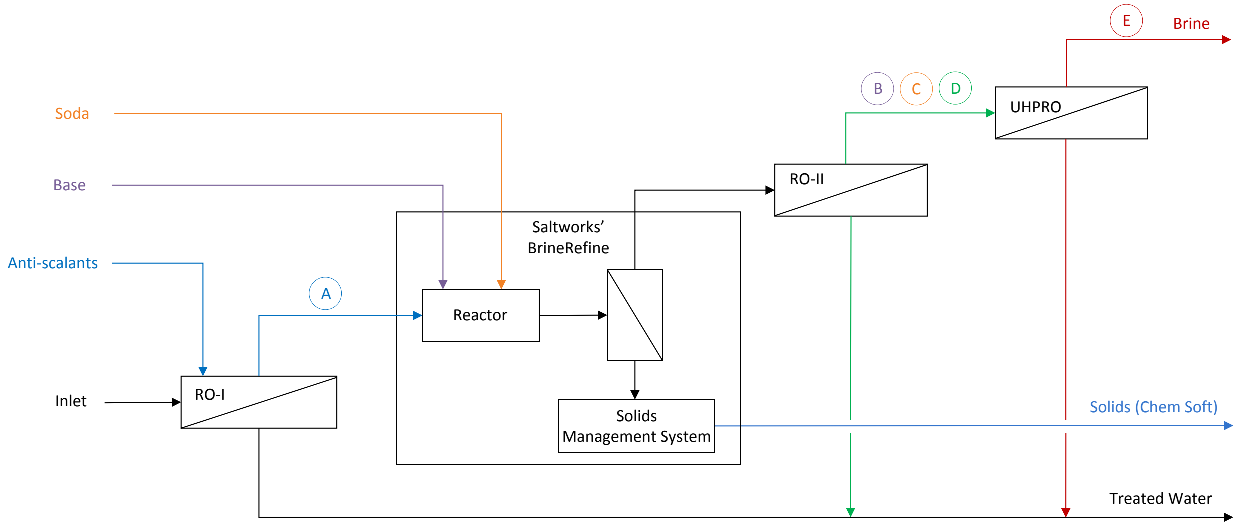
CASE STUDY: COOLING TOWER BLOWDOWN PILOT

Pilot tests on cooling tower blowdown water from a power plant were completed. The water was first concentrated at site by a primary RO achieving 80% recovery, which was then treated at increasing recovery in a flexible plant. Each recovery stage (volume reduction) is summarized in Table 2 and the PFD is shown in Table 2. The water chemistry emerging from each step is included in Table 3.

Table 2: Cooling Tower Blow Down Successive Recovery Increases

State Point	Volume Reduction	Recovery	Technology	Cost Guidance OpEx + CapEx ($\$/\text{m}^3$)
A	5X	80%	RO-I with anti-scalants, concentration polarization management, and flushes	\$1 - \$2
B	10X	90%	Above + high pH & RO-II	\$2 - \$3
C	20X	95%	Above + nominal soda	\$3 - \$3.5
D	40X	97.5%	Above + intense soda	\$3.5 - \$5.8
E	70X	99%	Above + UHP-RO	\$4 - \$8

Figure 2: Process Flow Diagram (PFD) showing Successive Recovery Additions



Although each step can be viewed as a unit operation, they should be treated as an integrated plant with unified and integrated process controls. This is recommended for the following critical reasons:

1. As feedwater chemistry and flow rates change upstream, an integrated plant can better react and adjust each unit operation accordingly.
2. Enable performance monitoring algorithms to be applied. This is done at both the plant and unit operation level, whereby upstream and downstream systems can communicate their performance and status to one another. Adjustments can then be made to achieve “best system efficiency”. A unified dash board should be included to assist plant operators and owners in monitoring performance.
3. Coordinate all process control design methods, control system design components, and programming style and documentation for both capital cost and operational cost efficiency (i.e., spares and maintenance).

In reference to Figure 2 simplified process flow diagram, water chemistry from a cooling tower trial is presented in Table 3. the brine concentration and composition changes with each incremental step in recovery improvement. Notice that the quantity of soda ash (sodium carbonate) dosing can vary, with the control mechanism being reached within 80% of calcium sulfate saturation in the brine for the desired recovery. Put another way, if higher recovery is desired, then more soda ash can be added. If lower recovery is sufficient, then less soda ash can be added. Soda ash chemical cost can be one of the higher operational cost inputs into a high recovery plant, and therefore, it should be controlled carefully. A real time calcium sensor was developed to measure calcium content at the inlet and adjust soda ash dosing to compensate. The objective is not to waste soda ash and generate excess sludge but also to not put the membrane system at risk. Operators aimed for 80% of saturation with anti-scalants employed, assuming anti-scalants can increase theoretical saturations by 3 to 4 times. In addition to the calcium sensor, a total dissolved solids (TDS) sensor was developed and used in thermal plants, but it may also be applied to the membrane concentration plants.

Table 3: Water Chemistry at Each Successive Recovery Increase

State Point	A	B	C	D	E
Recovery:	**80%**	**90%**	**95%**	**97.5%**	**99%**
Volume Reduction:	**5X**	**10X**	**20X**	**40X**	**70X**
Units:	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
pH (pH units)	6.90	5.92	6.23	6.56	6.79
Total Dissolved Solids	8660	18150	36790	76710	131000
Total Suspended Solids	<2	<2	<2	<2	<2
Total Hardness (as CaCO3)	4262	5047	6498	8986	15432
Total Organic Carbon	109	32.0	5	11	256
Alkalinity (as CaCO3)	100	1.77	30	15.1	28.5
Aluminum	1.27	0.03	0.06	0.11	0.19
Ammonia (as N)	1.57	1.89	3.78	7.56	15.9
Antimony	<0.005	<0.005	0.018	0.0324	0.0648
Arsenic	0.11	0.016	0.032	0.064	0.13
Barium	0.54	0.16	0.30	0.61	1.12
Bicarbonate (as CaCO3)	100	1.77	5.4	15.1	28.5
Boron	0.66	1.32	2.64	5.28	11.0
Bromide	54	108	216	433	865
Cadmium	0.00055	0.00039	0.00078	0.0016	0.0031
Calcium	660	1310	1190	661	1130
Carbonate (as CaCO3)	<1	<1	<1	<1	<1
Chloride	2250	4430	8860	18450	31630
Chromium	0.088	0.031	0.062	0.124	0.248
Cobalt	0.003	0.003	0.006	0.012	0.021
Copper	0.979	0.45	0.89	1.78	3.6
Fluoride	5.2	0.55	1.10	2.3	3.9
Hydroxide (as CaCO3)	<1	<1	<1	<1	<1
Iron	0.61	0.19	0.38	0.76	1.37
Lead	0.0101	0.0101	0.0058	0.01	0.02
Lithium	0.18	0.33	0.67	1.33	2.31
Magnesium	634	430	855	1780	3060
Manganese	<0.01	0.017	0.034	0.08	0.160
Molybdenum	0.55	0.58	1.16	2.32	4.62
Nickel	0.019	0.019	0.039	0.08	0.16
Nitrate (as N)	58.3	111	214	429	767
Nitrite (as N)	<0.05	<0.05	<0.05	<0.05	<0.05
Phosphate (Ortho)	14.5	0.11	0.22	0.44	0.75
Potassium	99.6	185	361	752	1289
Selenium	0.023	0.023	0.05	0.09	0.18
Silica (Reactive)	128	4.85	9.7	19.4	34.1
Silver	0.002	0.002	0.004	0.008	0.016
Sodium	1190	4090	9810	22520	38600
Strontium	4.98	6.25	12.5	26.10	44.7
Sulfate	3500	7580	15160	31590	54160
Zinc	0.091	0.091	0.182	0.368	0.736

Readers are offered the following reminders and guidance when considering brine treatment economics:

- Thermal system costs are >$20/m3, so although the advanced membrane brine system costs above may seem high to traditional potable water RO practitioners, these costs are still much lower than thermal brine concentration means.
- Sum the costs of chemical treatment and secondary RO, since the secondary RO would require chemical treatment to operate. For example, the net cost of a secondary RO may be $8/m3 ($4/m3 chemical treatment + $4/RO-II).
- Know where to stop: For example, if a brine disposal outlet is available for $5/m3, a primary RO system may offer economic advantages to concentrate brines but a secondary RO may not.
- Capacity matters: For smaller capacity plants, adding unit operations can add process and operational complexities. For example, if the brine flow rate from RO-I is 100 m^3/day and a thermal system is economic (i.e., disposal costs >$10/m3), it may make more sense to skip the secondary RO and proceed directly to the thermal system. This could be especially true if chemical treatment is avoided through use of an evaporator-crystallizer that does not require upstream pre-treatment. At higher brine flow rates, such as 500 m^3/day, a secondary membrane concentrator can be highly cost advantageous.
- Simple bench or pilot tests can considerably de-risk investments and offer pay back periods of weeks to months by enabling economic and process optimization of the system.

CONCLUSION

Advanced membrane brine concentration systems, data, and economics were presented. Methods were disclosed and pilot tested to achieve incremental volume reductions in brine, up to a 70 times volume reduction for a cooling tower blowdown stream. This was achieved by incorporating conventional RO, advanced chemical softening, and new ultra high-pressure RO membranes in systems designed to handle the feedwaters. Although each recovery improvement can be viewed as a unit operation, it should not. Integrated process control of the entire treatment should be practiced ensuring the system can operate reliably on variable feedwaters. A novel calcium and total dissolved solid sensor were developed by the authors to further assist operations on variable feedwaters. Economic factors were discussed, including “where to stop”, in an effort to guide readers in assessing the business case to implement the advanced treatment methods disclosed.

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