Modern Chemical Softening to Maximize RO Recovery: Scale Removal in Smart, Compact, Modular Systems

Takeaways:

- With the advent of ultra-high-pressure reverse osmosis and growing importance of brine management, modernized chemical softening systems can enable economic ultra-high recovery reverse osmosis, minimizing RO brine volume, disposal costs, and reliability risks.
- Chemical softening systems (Conventional and advanced) are described, including chemical dosing and tips on how to remove scaling risk.
- Conventional chemical softening settling times are reviewed as well as the risks posed by coagulant/flocculants that can foul downstream ROs.
- BrineRefine is introduced: an advanced chemical softening system that addresses many of the challenges faced by conventional chemical softening; there are no coagulants uses or foulants introduced (reduce ROI fouling risk); it is compact (no clarifiers), modular (minimal site installation); intelligently automated (precise dosing and recovery tuning); and includes a simplified solids management system to remove sludge management fuss.

Why care about scale?

As higher recoveries are pushed on RO systems, scale becomes the primary bottleneck to recovery improvements. As discussed in this RO blog, there have been many innovations within the RO field that seek to manage scale through operational 'tweaks' in order to achieve higher recoveries. The authors build such RO systems; they understand that operational tweaks and anti-scalants do not remove the underlying risk, but rather delay the symptoms. Operating at or beyond saturation limits means that any misstep could result in membrane fouling, decreased capacity, increased energy, plant downtime, and repairs. RO systems may also not be operated at their peak performance, leaving recovery on the table and wasting money on downstream more expensive brine treatment.

Before spending money to remove scale causing ions, consider which of the three categories you may fit in:

1. **Basic RO:** can achieve the desired recovery with basic RO and sound anti-scalant program (lowest cost).

2. **Advanced RO:** employ operational tweaks such as cycling concentrations while bleeding some brine, high cross flow, automated flushes and CIPs. This may push one to their recovery goal. In other cases, scaling risk may limit brine concentration and prevent achieving the maximum recovery achievable (system costs and complexity increases slightly).

Knowledge tip: maximum RO recovery is defined by osmotic pressure limits (the pressure at which water stops permeating through the membranes). New generation RO membranes can operate up to 1800 psi, or concentrate non-scaling fluids to 130,000 (NaCl) to 150,000 mg/L (Na2SO4).

3. **Chemical Softening + RO:** if done correctly, one can now truly maximize RO system recovery to reach the osmotic pressure limit. Scale causing compounds are removed by chemical softening as reviewed below, which also reduces the operational risk of membrane damage. However, one should only remove the right amount of scaling ions. Excessive dosing will result in excess chemical costs and sludge generation. Chemical softening typically costs \$2-\$5/m^3 inclusive of capital and operating costs, so is only worthwhile if the sum of chemical softening and a secondary RO are lower than the alternative brine disposal or thermal brine concentration costs (typically min \$20/m^3).

Design tip: assess the RO brine, and only remove the right amount of scale: we aim for 85% scaling potential of the downstream RO brine (with 100% representing the onset of precipitation).

If done correctly, scale removal will eliminate/mitigate the fundamental risk of precipitating on a membrane surface, allowing downstream systems to operate at high recoveries and greater reliability. Scale removal is most commonly carried out via chemical softening.

It is important to acknowledge that as water is concentrated, organics will also concentrate and they can foul an RO. In more severe cases, solvents concentrate to where they become insoluble and damage the RO membrane. This article focuses on scale removal to achieve ultra-high recoveries, but concentrated organics also need to be checked. Consideration of an organic removal "kidney loop" to treat out organics as they concentrate may be warranted. Nevertheless, do not fret too greatly about the organics as assessments can be completed. For example, contact the authors for more details.

Scale Management vs. Scale Removal:

The most important first step is to understand your water chemistry: the scale causing compounds it contains and concentration factor at which they will precipitate. Scale comprises low solubility salts that precipitate as water is concentrated. Precipitated salt, if uncontrolled, will plate-out on membranes. This impedes performance and decreases membrane life. Depending on water chemistry, different scale will pose different challenges. Figure 1 below is a "Periodic Table of Scaling Compounds" that shows the solubility of some of the most common scale compounds in industrial wastewater. Readers can use it to check the solubilities against their brine water chemistry.

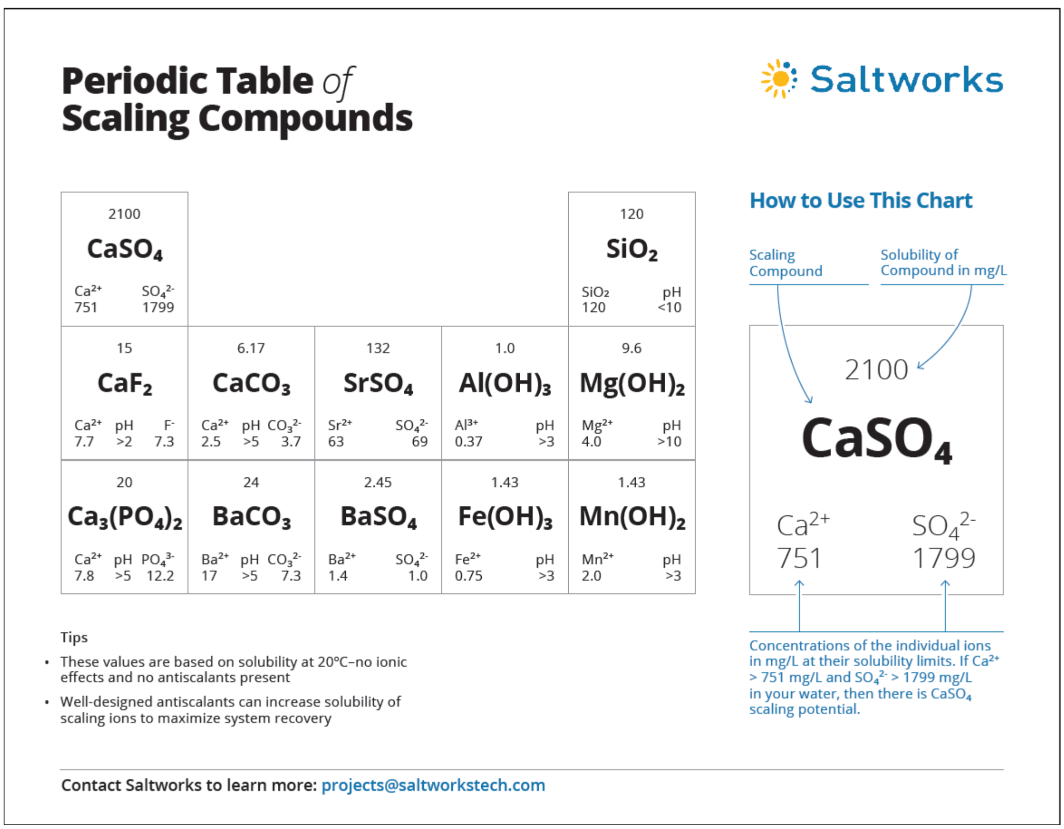


Figure 1: Periodic Table of Scaling Compounds

Calculation Tip: concentrated brine causes scaling, not the feed. So, concentrate your water chemistry individual ions by the same factor of volume reduction. For example, if operating at 75% recovery, that is 4X volume reduction, meaning all the ions in your water will be concentrated by 4X. Multiply your raw chemistry data by 4 and compare to the solubility limits in the periodic table of scaling compounds below. If two scaling ion pairs are both higher than the concentration in the table below, you could have scale form. Typically, anti-scalants can delay the formation of scaling by 2X above the theoretical concentrations below.

The most common scale encountered are typically: Silica, Calcium based salts, and metals (such as Aluminum and Iron). The table below discloses chemical methods to remove specific scaling ions.

Scaling Ion	**Chemical Removal 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 if req'd	20 – 80 mg/L
Ba	pH 9-11 + Soda Ash if req'd	< 1 mg/L (depends on initial Ba levels)
Sr	pH 9-11 + Soda Ash if req'd	< 5 mg/L (depends on initial Sr levels)
Mn and Fe	pH 9-11 / oxidation / greensand	
F	pH 9-11	< 2 mg/L
CO_3	pH 5	

Figure 2: Chemical Methods to Remove Scaling Ions

Conventional Chemical Softening 101 and Its Challenges

MVR Evaporators use a blower, compressor or jet ejector to compress, and thus, increase the pressure of the vapour produced. The increase in pressure results in an increase in the condensation temperature of the vapour. This vapour is then condensed in a heat exchanger, returning heat to the evaporating water in the next stage. This forms a cyclical process that recycles thermal energy, but requires electrical energy to run the large vapour compressor.

Conventional chemical softening systems have over 100 years of history. They are used throughout water treatment plants ranging from municipal to industrial wastewater. The process consists of:

1. Addition of lime to increase pH to 11 to precipitate out silica and heavy metals (aluminum and iron). Some calcium may also precipitate.

2. Addition of soda ash to precipitate out hardness ions (calcium, barium, strontium etc.) if the high pH step does not reach the calcium goal.

Steps 1 & 2 occur in large reaction vessels, often with a suspended agitator. Be cautious of mechanical forces on the agitator and ensure the metallurgy of the tanks and impellers will not corrode in your brine.

3. Clarification + Coagulants/flocculants to separate the precipitated solids and water (beware this step if RO is downstream).

Step 3 occurs in a clarifier, which may be vertical laminar plate type for smaller flows, or large circular type shown below. A higher solids brine settles to the bottom which is then directed to a filter press. The clarified fluid leaving the "top" clarifier is often directed to micro or ultrafiltration before an RO system. However, dissolve residual coagulants and flocculant byproducts will not be filtered and could foul the downstream RO.

4. Solids management step to handle the precipitated solids for disposal etc.

Step 4 occurs in centrifuges and/or filter presses, with the solids sent to landfill. Metallurgy and operability is extremely important, as is making sure the solids pass a paint filter test for landfill disposal (no free water droplets). If normally occurring radioactive material (NORMs) are present in the raw water, they may concentrate in the filter press solids and should be checked for radioactivity.

Conventional chemical softening, though effective, has some challenges when applied to modern RO systems

- **Fouling coagulant chemicals are added:** due to the poor settling nature of chemical softened solids, large clarifiers are required. The addition of flocculants/coagulants is often used to help decrease the size of clarifiers needed. See Figure 3 timeline photos of chemical softening solids settling without and with the aid of flocculants/coagulants. These specialty chemicals improve the settling of the solids by approximately 3X, reducing clarifier size by roughly 3X. However, iron and aluminum-based coagulants as well as polymers employed pose a fouling risk to downstream ROs: forming a gel on the membrane surface and requiring almost daily chemical clean in place (CIP) cycles. This common occurrence adds downtime, operator frustration, and increased chemical cost. One should not assume that 20-year-old chemical softening textbooks and design guidelines can be applied to RO systems, as these older systems were not designed for utilization with RO.

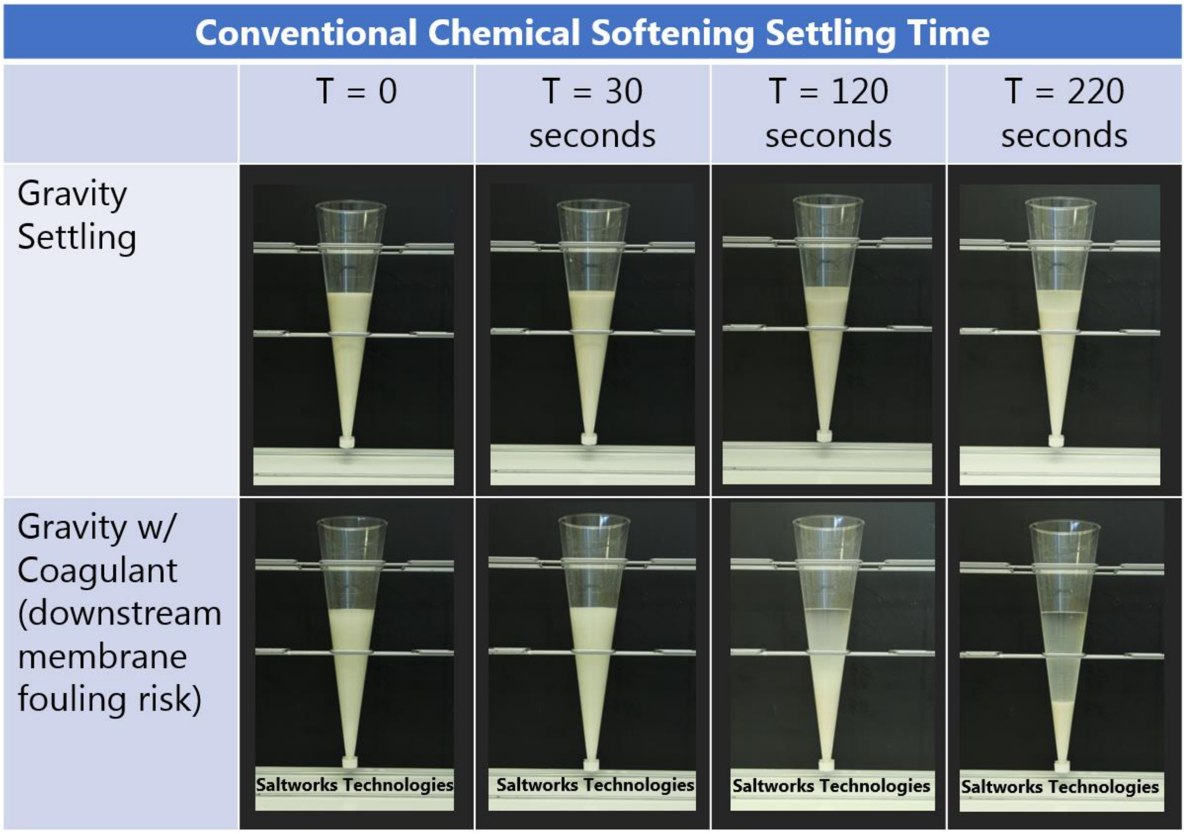


Figure 3: Conventional Chemical Softening Settling Time with and without Coagulant/Flocculant addition, by Saltworks

- **Large clarifiers** are employed to enable settling and downstream solids management. In higher hydraulic capacities, these need to be stick built at site, incurring higher installation costs and space requirements.
- **Imprecise chemical dosing;** the manual steady state nature of operating a conventional chemical softening plant means that there is higher risk of over-dosing chemicals (waste of chemicals) or under-dosing (scaling risk for RO as the scaling ions will not be adequately removed). If inlet water chemistry changes, so should the chemical dosing set points.

- **Solids and sludge management:** low flux filter presses are commonly used, resulting again in large equipment footprint and more frequent operator attention.

Tips:

- *Determine the most economic method/chemical for removal. Example: If there are high levels of sulfates, and magnesium in the wastewater, use of lime would be a lower cost option. However, if there are low sulfates and high levels of calcium, sodium hydroxide may be more cost effective if followed by soda ash softening. This is because sodium hydroxide does not add calcium, whereas lime will, resulting in increased usage of more expensive soda ash.*
- *Understand your solids disposal costs. Solid waste from the chemical softening process will also need to be disposed. The more chemicals added, the more solid waste is required for disposal.*

Advanced Chemical Softening: BrineRefine

Recent innovations have been developed focused on addressing the chemical softening challenges discussed above. BrineRefine, an example of advanced chemical softening, offers a safer, compact and smarter system for removing scaling ions at the optimal cost.

BrineRefine is:

- **No coagulants or flocculants:** no chemicals are added that could foul a downstream RO. Rather than use gravity and time to settle, BrineRefine includes a robust high flux mechanical separation step, producing filtered non-scaling brine suitable for direct feed into an RO system.
- **Compact:** BrineRefine eliminates the need for large reaction vessels and clarifiers. See Figure 4 below for BrineRefine solids liquid separation without the use of clarifiers or coagulants/flocculants.

Modern Chemical Softening Instantaneous Separation without Coagulation Fouling Risk		
	BrineRefine Pre-Separation (t = 0 secs)	Post Separation (Instantaneous continuous flow)
BrineRefine		

Figure 4: BrineRefine Solids-Liquid Separation without Clarifier and without use of Flocculants/Coagulants

- **Modular:** Without the need of clarifiers, BrineRefine consists of pre-built and tested ISO container sized blocks. Four 45 foot ISO container size blocks result in 600 m3/day capacity. Higher capacity plants add more "four packs." The modular and factory tested skids minimizes site installation, ensures quality, and provides economies of scale across as standardized factory built fleet, rather than higher cost project-by-project custom designs
- **Intelligent:** The controls are integrated with downstream and upstream unit operations to communicate changes in process conditions and allow the entire system to adjust to allow for maximum reliability. BrineRefine senses and reacts to changes in the feed chemistry, optimizing operation costs and downstream RO

recovery while providing the operator with remote control and simple human machine interface (HMI). Figure 5 is an example of how BrineRefine integrates controls with an RO system.

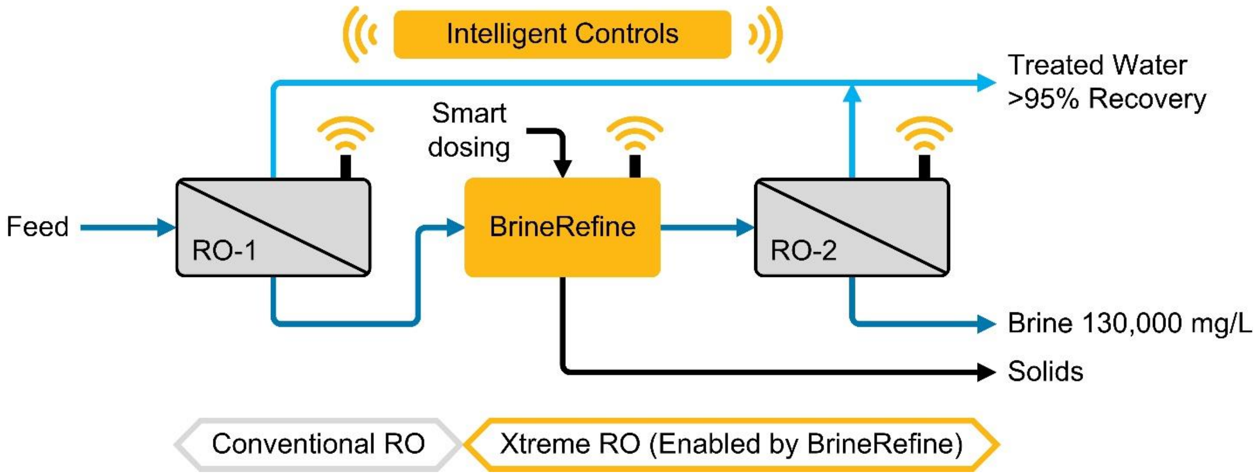
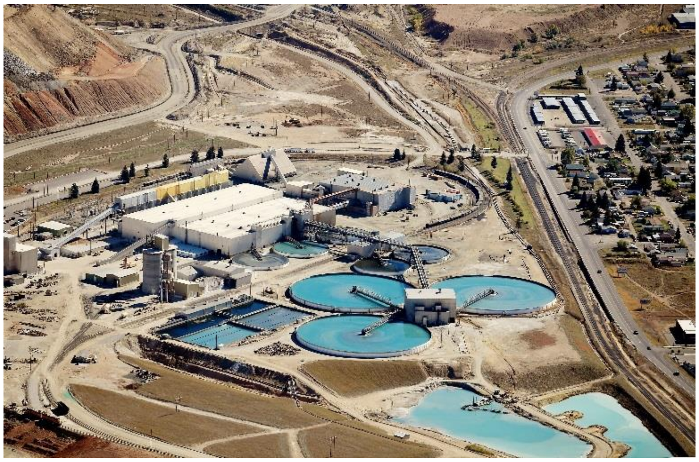
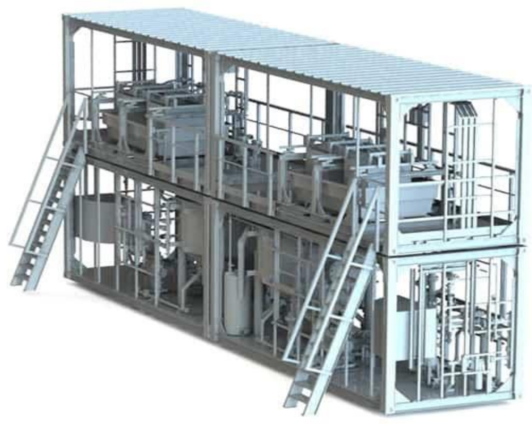


Figure 5: Integration of BrineRefine Controls with Upstream and Downstream RO

Single package: BrineRefine receives inlet feedwater, and outputs high quality filtrate that meets RO's SDI requirement, and filter cakes.

 Photograph of conventional chemical softening and the large settling clarifiers.	 BrineRefine ISO based double stack design, without large reaction vessels or clarifiers.

Pilot test units are available for BrineRefine, including both up and downstream RO systems as shown in Figure 5. A pilot is photographed below.

Figure 6: BrineRefine Pilot Unit

A case study is included below from a mine water treatment project. A primary RO could be used and was recommended by vendor A, however the client still sought further volume reduction. The primary RO could concentrate the brine to 50-55,000 mg/L total dissolved solids (TDS) with anti-scalants, but without chemical softening. At the ~55K TDS, calcium sulfate or gypsum scale could initiate. If according to Figure 5 above, the primary TO can be followed by BrineRefine and a secondary RO, further reducing brine volume in a membrane system by 2X (50% recovery = 50% less brine).

The secondary chemical softening and RO systems will be higher cost than the primary RO, but will be four times lower cost than a thermal evaporation system. The chemistry resulting from BrineRefine and the secondary RO brine is also shown below. Although calcium can be reduced to ~20 mg/L in BrineRefine, this target was not necessary. A lesser calcium reduction to ~135 mg/L was sufficient to ensure the downstream RO does not suffer gypsum fouling when concentrated to within 85% of the gypsum scale potential (i.e. calcium concentrating beyond 400 mg/L). The result is less chemical use and sludge generation, while still maximizing recovery and protecting the downstream RO.

Parameter	Primary RO Brine / Chemical Softening Feed	Chemical Softening Filtrate	Secondary RO Brine Reject
Units:	mg/L	mg/L	mg/L
pH	7.02	5.5	5.5
Total Dissolved Solids	51,400	50,850	130,000
Alkalinity (as CaCO3)	1101	501	1281
Aluminum	<0.25	<0.25	<0.25
Antimony	<0.06	<0.05	<0.05
Arsenic	0.06	<0.01	<0.01
Barium	<0.05	<0.05	<0.05
Beryllium	<0.005	<0.005	<0.005
Bicarbonate (as CaCO3)	<1	<1	<1
Boron	97.2	37.1	94.8
Bromide	31.4	30.4	77.7
Cadmium	<0.002	<0.002	<0.002
Calcium	1436	136	348
Carbonate (as CaCO3)	<1	<1	<1
Chloride	13,950	15,600	39,882
Chromium	0.105	<0.05	<0.05
Cobalt	<0.006	<0.005	<0.005
Copper	<0.06	<0.05	<0.05
Fluoride	<2	<2	<2
Iron	<0.5	<0.2	<0.2
Lead	<0.005	<0.005	<0.005
Lithium	1.65	1.35	3.45
Magnesium	1860	41	105

Parameter	Primary RO Brine / Chemical Softening Feed	Chemical Softening Filtrate	Secondary RO Brine Reject
Units:	mg/L	mg/L	mg/L
Manganese	<0.06	<0.03	<0.03
Mercury	0.015	0.003	
Molybdenum	0.915	0.72	1.84
Nickel	<0.06	<0.06	<0.06
Nitrate (as N)	58.8	58.7	150.1
Nitrite (as N)	<0.06	<0.6	<0.6
Phosphorus	6.3	14.4	36.8
Phosphate (Ortho)	0.47	0.009	0.023
Potassium	27	28.5	72.9
Selenium	0.0034	0.0028	0.0072
Silica (Reactive)	53	1.09	2.79
Silicon	67.5	<3	<3
Silver	<0.03	<0.03	<0.03
Sodium	15,600	21,600	55,221
Strontium	57.2	0.705	1.802
Sulfate	17,625	12,675	32,404
Thallium	<0.002	<0.002	<0.002
Tin	<0.005	<0.005	<0.005
Titanium	<0.1	<0.1	<0.1
Uranium	0.2895	0.156	0.399
Vanadium	<0.1	<0.1	<0.1
Zinc	<0.5	<0.5	<0.5

Every industrial water treatment project, chemistry and goals may differ. It is important to understand the economics of brine management and cost of each option. Do not spend more money concentrating brine than the savings that would be achieved from reduced disposal. For example, if it costs $5/m^3 to achieve ultra high recovery with an advanced chemical softening and RO system, that should only be done if the brine disposal costs are greater than $5/m^3. Thermal systems are at least 4X more costly than $5/m^3, so advanced membrane systems make a lot of sense to pre-concentrate before an evaporator.

In addition to understanding your chemistry, one must also think about variability. A good way to do this is to take water samples at periods of both high and low flow and send them into a lab for detailed chemistry analysis such as the one above.

Finally, although there many vendors and options on how to package both chemical softening and reverse osmosis, look for a company who does it frequently. Engineers can read online design guides and advise on different mechanical design options, but lessons learned from those with past implementation experience can be invaluable and save your project repeating mistakes of the past. Vendors with modular designs developed for repeat dispatch may have a more mature and battle tested product line. These vendors are available to help you understand your total cost of ownership (capital plus operating cost) and assess if membrane brine concentration is worth it.

Please feel free to contact Saltworks (projects@saltworkstech.com) for a detailed review of your project, risk and opportunities, as well as options to limit your brine management costs.

