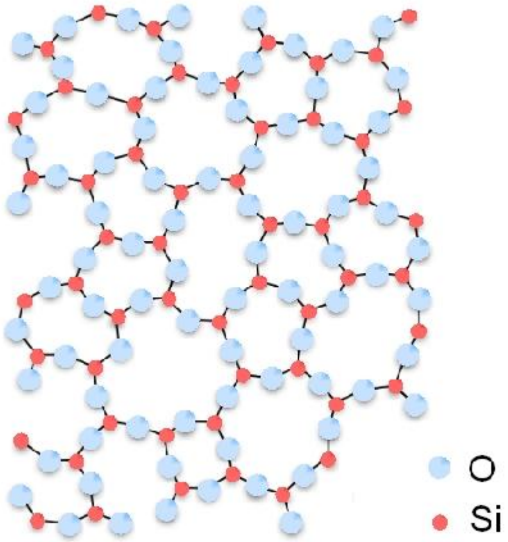
Slaying the Silica Dragon with Vibrating Membranes; *a Paradigm Shift in Brine Minimization*

Executive Summary

Provided one is not directly adjacent to a saltwater disposal point, RO brine disposal is problematic and expensive. Brine concentration in traditional reverse osmosis membrane systems is limited by the amount of silica in the feed water. VSEP's vibratory oscillation prevents silica fouling, and thus VSEP is ultimately limited by osmotic pressure, not silica. Because of this unique capability, VSEP has become the market leader in non-thermal brine minimization.

Background

Open any membrane system design program and you will quickly learn that much of the software package is written around silica. Under no circumstances may we allow it to precipitate, we fear, for it will wreak havoc throughout the system and render it useless. In the context of brine minimization, the fear of silica precipitation is ever-present. Rather than a few ppm, silica levels here are in the hundreds, and we justify extreme chemical alteration of the feed just to wring out a few more drops of clean water. Or on the other extreme, we give in to silica—let it all pass through—don't hold it back, and don't concentrate it.



Silica structure, courtesy Wikimedia Commons

The fear of precipitation is of course all too real for operators of traditional membrane systems—silica truly is a monster awaiting its super-saturated awakening. The presence of silica forces us to back off on recovery, add advanced antiscalants, change the pH, and clean more often than we'd like. In short, silica has ruled the lives of engineers and operators for more than fifty years—living in fear of its ability to turn pristine membranes into sheets of glass. But it needn't be this way.

Rather than altering the chemistry of brine, membrane technology firm New Logic Research altered physics. Its vibratory shear-enhanced process (VSEP) membrane separation system had been around since 1987, but the technology was never specifically applied to brine. The system was originally geared toward difficult-to-concentrate chemical slurries (mostly with microfiltration and ultrafiltration) where the torsional oscillation of the membranes kept the colloidal solids hovering above the membrane surface rather than allowing them to deposit on the membrane. Could VSEP's torsional shear have a similar effect on dissolved inorganic scaling components like silica? Research would soon show it could.

But before we get into the specifics of VSEP's silica-fighting abilities, let's ground our understanding by exploring the technological landscape of brine minimization as it stood before VSEP's entry into the field.

Being an inherently difficult application, brine minimization options are few, and historically included the following:

1. Evaporation Ponds
2. Thermal Evaporation
3. Hauling to off-site disposal
4. High Efficiency Reverse Osmosis (HERO)
5. Electrodialysis Reversal (EDR)

Let's examine each approach and understand the impact of silica.

Solar Evaporation Ponds

Perhaps the most simplistic approach to brine disposal is to put it outside and wait for the sun to make it disappear. Solar evaporation tends to be used in hot, arid locations where land is relatively inexpensive. Properly engineered evaporation ponds have strict limitations on permitting, construction, and operation, however. Ponds must be correctly sized, properly lined, and made to adequately protect area wildlife, for example.

Pond liner installation, photo courtesy GDT Lining

Ponds are not designed around silica, but there can be scaling issues in the systems used to convey the brine. Assuming the pond is large enough to handle the brine flow and the expected evaporation rates are achieved, it should work as expected. But even ponds need regular maintenance (particularly dredging of salts that build up within) therefore solar evaporation ponds are often designed with redundancy to allow for downtime.

Given that ponds need to be situated in warm, arid climates where land is cheap, it's a relatively rare option that becomes more so as flow rates rise. And should weather patterns change, a pond may quickly run out of room, forcing the operator to employ emergency (read: confiscatorily expensive) contingency plans to regain precious freeboard.

Thermal Evaporation/Crystallization

Much like solar evaporation, thermal evaporation aims to make the brine disappear. Rather than using free solar energy, however, electricity or steam are employed. The basic unit operations here are evaporators, which boil the brine to create steam and concentrated brine, and crystallizers, which drive the salts out of solution through further heating.

Evaporator installation, photo courtesy MarketWatch.com

Evaporators can concentrate brine up to about 300,000 ppm TDS (30%) by recirculating the brine through a shell and tube or other arrangement. If zero liquid discharge (ZLD) is required, the concentrated brine is sent to a crystallizer to precipitate the solids out of solution through higher temperature heating.

Depending on the nature of the precipitated solids, they may be centrifuged or processed in a filter press prior to disposal. The steam generated can be discharged or recovered as distilled water for reuse.

There is no debate over the effectiveness of thermal evaporation, but the approach is not without its drawbacks. The number one complaint is cost. Evaporators can be quite large, and must be made of costly corrosion-resistant metals like titanium, so capital costs are necessarily high. Likewise, operating costs are high because of the energy required to boil the brine, roughly $20/1,000 gallons for multiple effect evaporators. Scaling can also be an issue as well as corrosion of the exotic metal parts.

That said, where zero liquid discharge (ZLD) is required and disposal is not an option, thermal systems are often the best way to get brine to a dry solid. By pairing VSEP with novel thermal technologies, one can drastically reduce the size of the evaporator/crystallizer to reduce both capital and operating costs.

Hauling

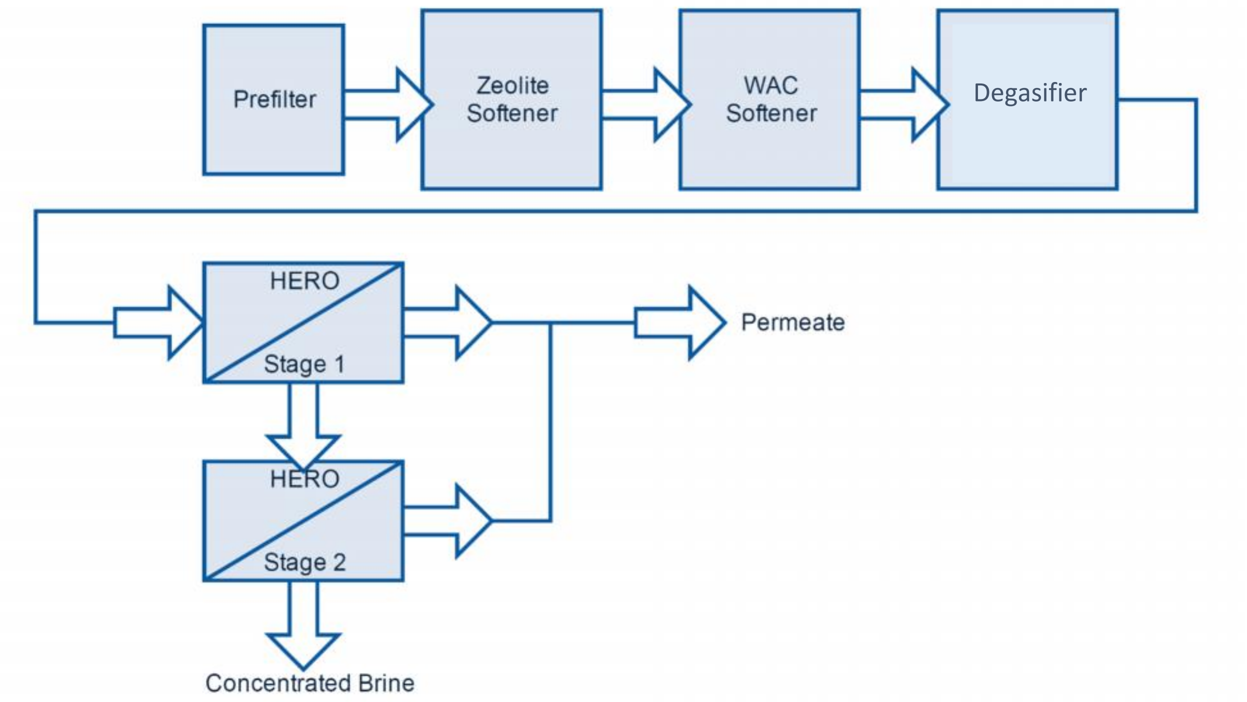
The ultimate no-brainer brine disposal technique is hauling. Put the brine in a tank, pump it into the truck and away it goes. Of course, the brine hauler still has to dispose of the liquid somehow, and their choices typically include a brine line to the ocean, a deep well injection site, an evaporation pond, or thermal evaporator/crystallizer.

As the brine generator, you are now paying for the hauling as well as the disposal. As such, capital costs are nil aside from the brine tank, but on the other hand, operating costs are extremely high. If brine production is ongoing, it therefore behooves the generator to invest in on-site treatment equipment. The return on investment can be quite rapid—especially when hauling distances are significant, and the water savings allows the company to burnish its sustainability credentials.

Photo Courtesy Marcellus-Shale.us

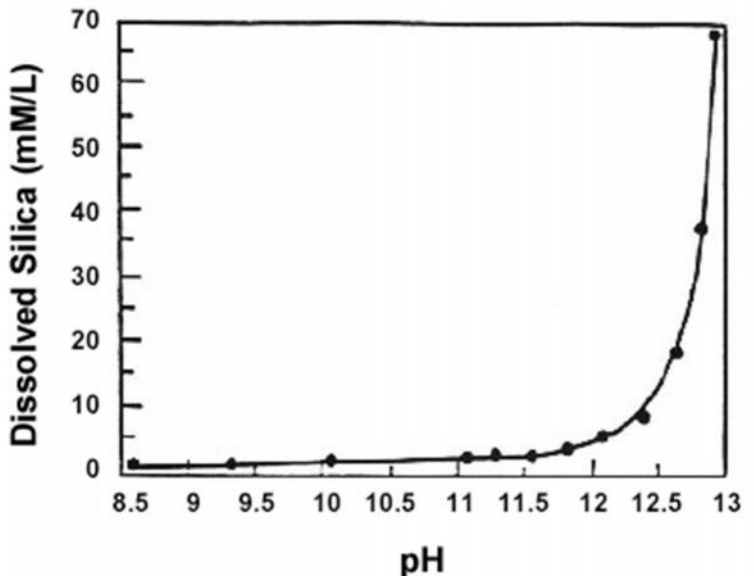
HERO

High Efficiency Reverse Osmosis (HERO) is a multi-step treatment process developed in 1996 as a high-yield ultrapure water system for the microelectronics industry. The system is designed to allow reverse osmosis membranes (RO) to operate at high recovery in the face of difficult-to-treat feed waters by removing foulants prior to the RO, and running the RO at high pH to keep silica in solution.



Simplified HERO Process Diagram

The first step in the process is to raise the pH with caustic, after which the feed is sent through a zeolite unit and a weak acid cation exchange unit (WAC) to soften the water. The cation resin exchanges the hardness ions for hydrogen ions, which reduces the pH of the feed water and converts the alkalinity to carbonic acid and carbon dioxide. Additional acid is then added to complete the conversion of any remaining hardness to CO2, which is subsequently removed in a degasifier. After the feed is degasified, more caustic is added to raise the pH to ~10.5, which increases the solubility of the silica. Once these steps are completed, the feed is introduced to the RO stages. Interestingly enough, even with this elaborate pretreatment, HERO's recovery is still limited by the silica solubility.



Silica solubility vs pH, Courtesy US DOT

Looking at the unit operations of the HERO process, it becomes apparent that despite being characterized as a membrane-based solution, the majority of the work is actually accomplished upstream of the RO. After adding sodium hydroxide to the feed solution, sodium, calcium and magnesium are deposited on the ion exchange resin, and there it stays until removed with an equal molar amount of hydrochloric acid (a process called regeneration). Given that the waste stream created from the regeneration process contains all of these various salts from the feed, it would appear that the real exchange provided by the WAC is not hardness for hydrogen, but sodium for silica.

Stepping back for a moment, one cannot help but ask why ion exchange, a technology normally reserved for polishing applications, is being used as the frontline unit operation in a high TDS environment? The answer is actually in the introductory paragraph to this section. HERO was developed to treat ground water with high silica levels, not wastewater. In the context of high TDS wastewater like RO brine, the resin would be loaded quickly and require frequent regeneration. What is not mentioned in the HERO literature is that additional physical/chemical pretreatment ahead of the WAC is often necessary to avoid near-continuous regeneration of the resin.

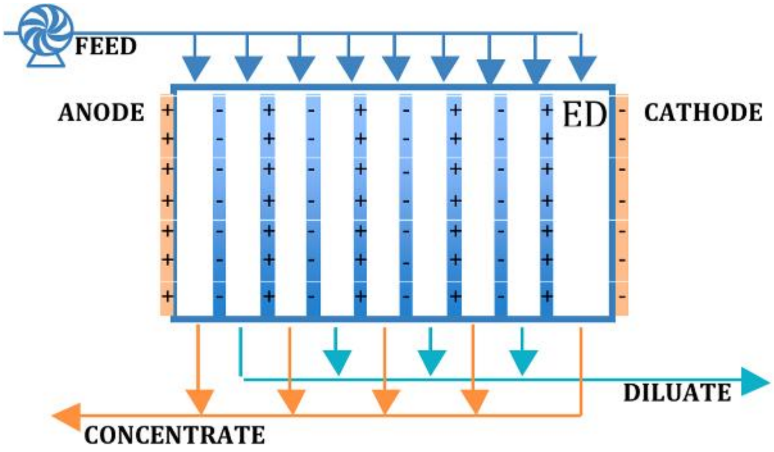
EDR

GE EDR system, courtesy Hydroscience Engineers

Electrodialysis reversal (EDR) is another technology deployed when silica levels are too high for conventional RO systems. But EDR's silica-specific selling point isn't that it concentrates silica, it's that it doesn't. EDR's rigid ion exchange membranes send ions packing, but allow silica to pass right through.

EDR works by applying electricity to alternating stacks of cationic and anionic exchange membranes, which selectively drive the compounds through the membranes to the side with an opposite charge. Insodoing, a product stream and concentrate stream are created.

The "reversal" comes as the polarity of the electricity is flipped periodically to discourage fouling of the media. Despite the polarity reversals, fouling still occurs, and periodic cleaning with strong hydrochloric acid is necessary to dislodge the foulants.



EDR diagram, courtesy mines.edu

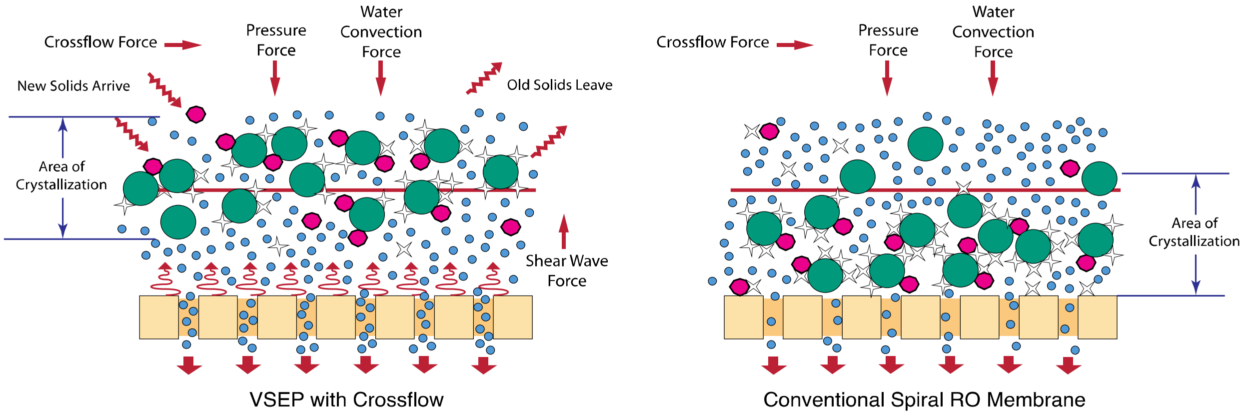
EDR's electrical inputs dictate its economic viability. Too little TDS, and RO would be cheaper. Too much TDS, and the electrical acid regeneration costs are too high. The sweet spot for EDR is in seawater desalination, where the technology has been most widely applied (It is commonly used in Japan to simultaneously generate fresh water and table salt).

As the TDS increases in the feed, so must the electrical input; soon one runs into a case of diminishing returns. And as with HERO, much of the "work" in the process is performed by the upstream equipment: flocculation/sedimentation and clarification in this case. And like other membrane systems, the EDR membranes must be replaced periodically.

VSEP

Vibratory Shear Enhance Process (VSEP) was developed in 1986 by New Logic Research Co-Founder, Dr. J. Brad Culkin. Originally designed as a blood separator for an in-office analytical apparatus, VSEP was subsequently scaled up and applied to the world of chemical processing, water and wastewater treatment.

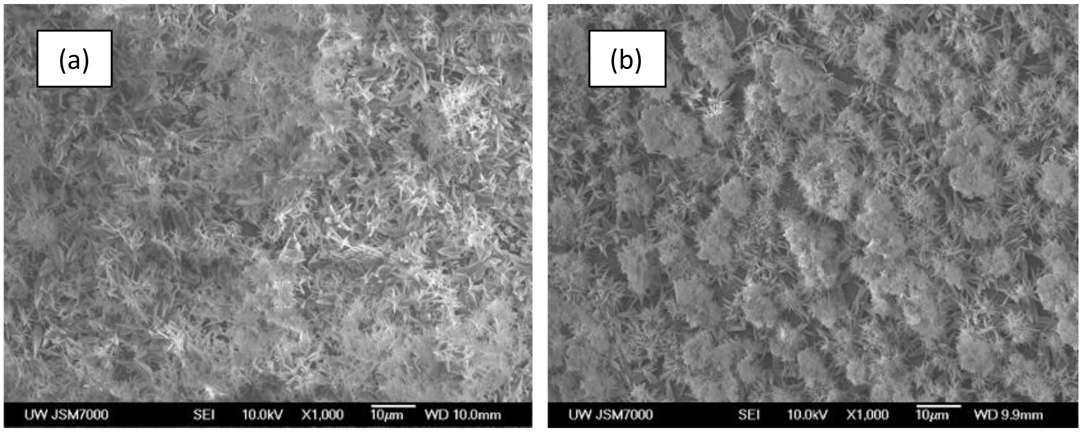
VSEP uses vibratory shear to prevent fouling of the membranes, which allows it to be used in a variety of difficult separation applications. By oscillating the filter module fifty-four times per second, solids are strongly discouraged from attaching to the membrane surface.



VSEP vs. Crossflow membrane systems comparison

For RO reject treatment, VSEP uses the same thin film polymeric membranes found in spiral-would reverse osmosis membrane systems, but they are deployed in a very different way. The membranes are attached to evenly spaced discs rather than tightly wound around a spacer, thus solids can easily exit the system whether they arrive as suspended particles, or *become* suspended through chemical precipitation. And because the shear is created by mechanical vibration rather than the feed pump, VSEP can achieve up to 90% recovery in a single pass. By arranging VSEP systems in series, recoveries greater than 99% are attainable.

Operators of traditional membrane systems stop concentrating SiO2 at 150 ppm because at 200 ppm, their membrane modules would become irreversibly coated in silica. Scanning electron microscope photographs clearly show the uniformity of the silica deposition, and it's this homogeneity that renders the fouling permanent. Without any open pores to begin the clearing process, even aggressive chemical cleanings are useless.



SEM images (top view) of post-test RO membranes (a) Without vibration; (b) With vibration.

While VSEP is not completely immune to silica scale, silica takes much longer to attach to the membrane, and when it finally does, the deposition pattern on the oscillating membrane is not uniform. Because of this, standard VSEP membrane cleanings are highly effective in removing the silica deposits.

> *"Vibration of RO membranes in an L-mode VSEP system reduced fouling in treatment of both a brackish solution and a brine. SEM images indicated that the entire membrane surface was covered with a uniform layer of needle-like crystals in the absence of vibration. When the membranes were vibrated, the scale in the brackish water system changed from a collection of needles to a smooth, continuous, but perforated, layer, and in the system fed brine, it changed to discontinuous groups of clumped needles. In both cases, those changes opened up areas of the surface and allowed the overall volumetric flux to increase."*
> *Evaluation of VSEP to Enhance Water Recovery During Treatment of Brackish Water and RO Concentrate –Mark M. Benjamin, Wei Shi, Pierre Kwan, and Yujung Chang*

Without a silica limitation, VSEP can continue concentrating brine until the osmotic pressure of the solution rises to a level at which it can no longer permeate the membrane. In standard VSEP systems, maximum feed pressure is 550 psi, while the high pressure VSEP systems operate up to 1,000 psi. Given that it takes 100 psi of feed pressure to permeate RO membranes with a 1% salt solution, VSEP can therefore concentrate brines up to 5.5% in its standard systems and 10% in its high pressure systems before being limited by osmotic pressure.

By going from 550 psi to 1,000 psi, VSEP moves from the category of brine concentrator into the realm of crystallizer, as multivalent salts are driven out of solution. If zero liquid discharge (ZLD) is required, VSEP's 10% brine makes for cost-effective hauling or feedstock to thermal processes.

Conclusion

In most brine minimization applications, options are few. Non-coastal disposal is difficult, direct thermal systems are large and expensive, and membrane-based systems including EDR and HERO are limited by silica in the feed.

Standing in contrast is VSEP, which is limited only by osmotic pressure. In fact, New Logic Research has installed VSEP systems to further concentrate brine generated by both HERO and EDR systems at full scale. It is VSEP's ability to act as a brine concentrator and multivalent salt crystallizer that has made it the leading choice for non-thermal brine minimization around the world.

Plant operators and engineers looking to increase water recovery, improve sustainability, and reduce brine disposal costs are increasingly turning to VSEP to solve these complex challenges with a quick ROI. For more information on how VSEP can help you meet your brine minimization and sustainability goals, please contact:

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VSEP RO Reject Installation, Inner Mongolia, PRC / Photo Courtesy Edwin Wong