

# **Kinetics of Mineral Scale Membrane Fouling**

## **A Comparison of Conventional Crossflow Membranes and V $\diamond$ SEP, a Vibratory Membrane System.**

Greg Johnson<sup>a</sup>, Dr. Brad Culkin PHD. <sup>a</sup>, Michele Monroe<sup>a</sup>

<sup>a</sup>New Logic Research, Incorporated  
1295 67<sup>th</sup> Street, Emeryville, CA 94608

Presented :

Keywords: Membrane, Fouling, Mineral Scale, Solubility Limits, Scaling Control, Reverse Osmosis, Filtration

### **Abstract**

Polymer Membrane Filtration is often used for water treatment. During the filtration process, very clean water is obtained as the permeable membrane allows very small nuclei to diffuse through it when pressure is applied. Suspended colloids, inorganic salts, dissolved organics, and other disassociated species are rejected. The benefit of membranes is the accuracy of the separation process and the high quality of filtrate that can be recovered. One of the limitations on membrane performance is that the permeate rate can be reduced by fouling or blinding of the surface. This can occur in several ways including charge association, hydrogen bonding, hydrophobic interaction, or from exothermic chemical precipitation of sparingly soluble earth metal salts which can occur at the membrane matrix. This paper investigates the initiation mechanisms and effects of mineral scale formation in membrane systems and compares the benefits of using a vibrating membrane system such as the V $\diamond$ SEP, (Vibratory Shear Enhanced Process), to the use of conventional crossflow membranes.

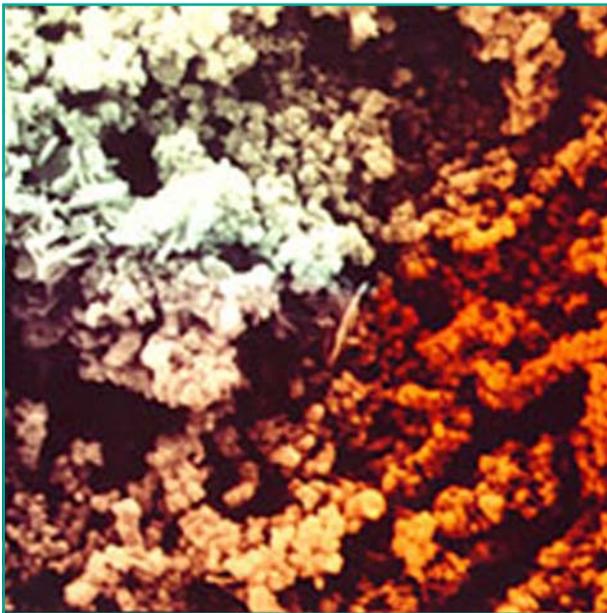
Other studies have shown the benefits of V $\diamond$ SEP when it comes to the Ultrafiltration process and its ability to mitigate the potential effects of organic fouling and diffusion polarization of the membrane surface. This study will investigate benefits of V $\diamond$ SEP on a molecular level with regard to spontaneous chemical bonding that can occur in Nano-Filtration and Reverse Osmosis membranes.

The focus of study is on the effects of mineral scaling in membrane systems. During the filtration process the solubility limits of slightly soluble salts can be reached and the salts will then precipitate out as crystalline mineral scale; forming additional suspended colloidal which poses a threat of fouling. The study demonstrates the resiliency of V $\diamond$ SEP with respect to mineral scale formation and the lack of need for pre-treatment with anti-scalants or other chemicals to inhibit crystal formation and growth.

## Background

Membrane fouling and scaling can significantly increase the cost of a membrane system as well as reduce its reliability. This limitation has been the cause of a great deal of recent development in membrane science. Several approaches have been used to try and minimize the effects of fouling.

Polymer chemists are developing many new membranes that have “low fouling” characteristics. Several techniques are used like altering the Zeta Potential or amount of ionic charge of the membrane surface. Another method is modifying the thermodynamic potential of the membrane surface by using low surface energy materials that reduce the chemical free energy change upon absorption of foulants.



### MINERAL SCALE FOULING OF A MEMBRANE

Other developments have focused upon offering the potential foulants an alternate site for chemical attraction, or limiting their rate of precipitation, so these foulants are used up or diluted in their effect and thus will not pose a threat to the membrane itself. Examples of these are “anti-scalants” which can be organic compounds with sulfonate, phosphonate, or carboxylic acid functional groups. Also used are chelating agents which sequester and neutralize a particular foulant. Carbon, Alum, and zeolites can be used. They offer huge surface areas loaded with nucleation sites suitable for absorption or crystallization to occur spontaneously at relatively low solubility levels.

Another method of combating fouling is by affecting the fluid dynamics at or near the membrane surface. “Crossflow” membrane systems employ aggressive tangential flow in order to help reduce the thickness of diffusion polarization layers of foulants, as well as colloidal films that can form on the membrane. Since static dead-end media will simply retain particles or ions left behind as the water is removed, it is only a matter of time until the rejected material must be physically removed. Cartridge filters and bag filters work in this manner. Crossflow membranes employ the use of turbulent flow across the membrane surface to “wash” away the particulate matter that is deposited, and to depolarize the membrane. Vibrating membranes, such as V $\diamond$ SEP, use crossflow in addition to the increased shear caused by torsional oscillation of the membrane itself to repel suspended solids.

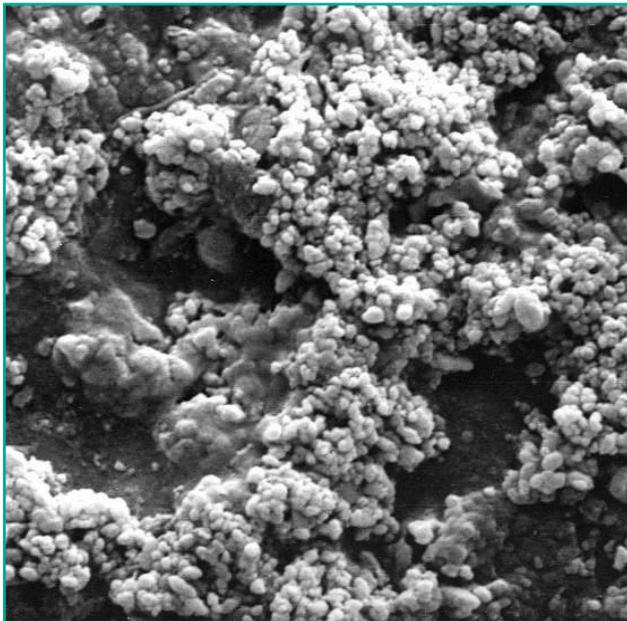
Most often, the optimum membrane system will employ several of these developments in order to combat fouling. For example, crossflow membrane systems will utilize pre-treatment of the feed water by using a 5.0 $\mu$ m bag filter followed by a 1.0 $\mu$ m Cartridge filter. Then the system will use a “Low Fouling” membrane with advantageous surface chemistry. An antiscalant will be dosed into the feed to sequester any potential foulants. And finally, aggressive crossflow is used to keep the membrane clear. This is a suitable treatment process as long as the feedwater is within specific criteria including LSI (Langolier Saturation Index), and SDI (Silt Density Index), amounts of sparingly soluble salts and other suspended colloids.

## Introduction

Membrane filtration using Reverse Osmosis and Nano-Filtration has been proven as a very effective technology for the removal of dissolved solids including toxic substances from industrial wastewater. It can also provide a source of ultra-pure water for chemical processing, manufacturing, and for drinking water. The results of the filtrate quality are predictable and reliable. The filtrate quantity that results from a membrane system is more difficult to predict. There is no reliable method for predicting either the rate of fouling or the extent of it. This can lead to miscalculations in system sizing and unreliable performance. One way to minimize this risk is to over design a system with ample turn down ratio and also to minimize fouling or the mechanisms for fouling.

One type of membrane fouling comes from mineral scale which can crystallize and grow at the membrane surface leading to a loss in performance. Eliminating mineral scale as a possible membrane foulant greatly reduces the rate of fouling of any membrane system. The conventional method of controlling membrane scaling is to use synthetic organic compounds and polymers, or anti-scalants, which work to inhibit the growth of crystals. While somewhat effective, these chemicals do have certain limitations and drawbacks.

Addition of these chemicals to the feed waters of the membrane system increases the amount of waste, which is problematic from an environmental point of view. The exact dosing is not exactly known and so overdosing is needed to ensure successful use. Anti-scalants must often be tailor made for various scaling components. The chemical addition adds to the operating costs of a membrane system, increases its complexity, and adds liability with regard to worker safety and discharge. Phosphonate anti-scalants can lead to bio-fouling of the membrane as the presence of phosphorous promotes biological growth both in the membrane system and in the sanitary discharge system.



**ORGANIC BIO-FOULING OF A MEMBRANE**

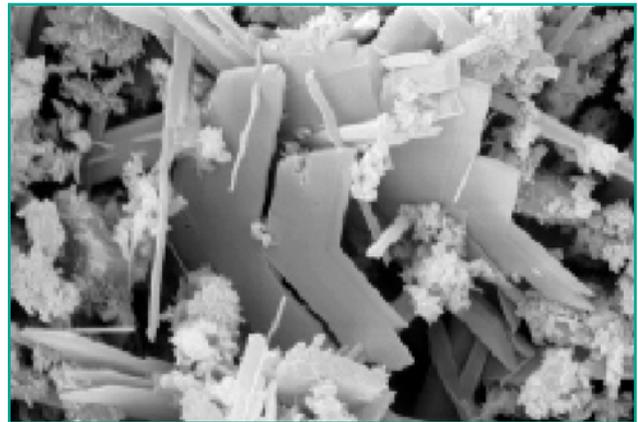
This can put an unnecessary load on local POTW treatment plants. Although anti-scalants are effective at reducing mineral scale formation on membrane surfaces there are other effective non-chemical methods more desirable.

## Types of Mineral Scale

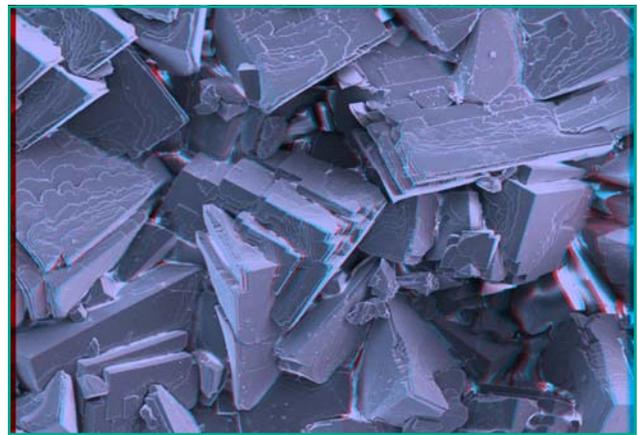
Minerals that will precipitate and form scale as they come out of solution are predominantly composed of divalent metal ions. Monovalent metals such as Sodium and Potassium are nearly completely soluble, whereas, in the presence of Sulfate, Phosphate, or Carbonate, divalent ions such as Calcium, Iron, Magnesium, Barium, Strontium, Radium, Beryllium, Lead, and Silicon are nearly insoluble. As these molecules precipitate, they form crystals that begin at a nucleation site.

Common forms of mineral scale include:

- Calcium Carbonate
- Calcium Sulfate
- Calcium Phosphate
- Barium Sulfate
- Strontium Sulfate
- Iron Hydroxide
- Silicon Dioxide (Silica)



**CALCIUM SULFATE CRYSTAL**



**CALCIUM CARBONATE CRYSTAL**

## Equilibrium and Solubility

“For every action, there must be an equal and opposite reaction” In stoichiometric chemistry calculations, it is assumed that the reaction runs to completion. In actual fact, a chemical reaction is a continuous state of equilibrium. Each chemical reaction has its own constant ratio of reactants and products. A reaction may “look” finished when equilibrium is reached, but what is happening is that forward and reverse reactions are occurring simultaneously. Such is the case for partially soluble solutes in a solvent.

Le Chatelier’s Principle states that if a system at equilibrium changes, the system will shift its equilibrium to compensate for the change. Each ionic compound will have its own solubility limit. This is the maximum amount of component that can remain dissociated in solution. This is measured in g/L and is identified as  $K_{sp}$  (solubility product constant). The solubility constant is dynamic and can change with temperature, pressure, and pH swings.

There are several states also affecting the solubility of compounds. If the amount of reactants is well below the total amount that can be dissolved in solution, (below the solubility limit), the solution is said to be dilute. In this case little or no precipitation will occur. As the concentration of the reagents increases and nears the solubility limit, the solution is said to be a saturated solution. If the amounts of reagents are above the solubility limit, the solution is “supersaturated”. Around the solubility limit exists a zone known as the “metastable” range. This is a range of solubility levels at which precipitation can occur if certain conditions exist in favorable ways.

Phase changes occur at liquid/solid interfaces. These reagents will look for nucleation sites to assist in the initiation of the precipitation process. In systems with a lot of liquid/solid interface full of nucleation sites, precipitation can occur readily at the lower end of the metastable range of solubility. For systems with small surface to liquid ratios or for surfaces low in surface energy or nucleation sites, the solubility of reagents must be increased to the super saturated condition since access for the reagents to a favorable reaction site are limited. Another factor is time. Precipitation occurs at a finite rate determined by the number of sites, the degree of saturation, temperature, pressure, and many other variables.

## Chemical Thermodynamics

The First Law of Thermodynamics states that energy cannot be created or destroyed. Energy can only change its form. Heat and Work are interchangeable forms of energy. Heat can produce Work and Work can produce Heat. For example, steam drives a locomotive and the brakeshoe of a railcar produces heat. Energy is stored in materials is known as potential energy.



### POTENTIAL & KINETIC ENERGY

**A Roller Coaster is an example of Potential Energy and Kinetic Energy. Energy converted to work as the car is pulled to the top is stored and released as the car reaches the crest**

Chemical reactions occur if the free energy is reduced overall. Chemical precipitation will occur if the reagents have reached their solubility limit and if the reaction represents a favorable free energy change incrementally, i.e. “on the margin”. By way of analogy, the water in a mountain lake can reduce its free energy by flowing down hill. It does not do so because incrementally, it must first flow up hill over the banks of the lake before going down hill. The process is halted because locally, incrementally, “on the margin” the change in free energy is increasing not decreasing, so nothing happens. The same thing can happen in chemical systems when crystals or bubbles are forming.

Consider a supersaturated solution of Carbon Dioxide in water like champagne. The bubbles of gas come out of solution only at specific locations on the wall of the glass. The small number of formation sites limits the rate of gas evolution allowing the beverage to stay “fizzy” for hours. Almost everywhere in the system, for a bubble to form, locally, incrementally, and “on the margin” the free energy must first increase to form a bubble. Therefore nothing happens.

Specifically, suppose a very small bubble did appear in the middle of the glass, away from the wall. This tiny bubble will have a surface tension as all liquid gas interfaces do. The pressure inside any gas bubble is twice the surface tension divided by the radius of the bubble. For a newly forming bubble, this pressure is therefore very high (one over  $R$  is a big number), but if the gas pressure is higher than the pressure that was originally used to supersaturate the liquid, not only won't the bubble grow, it will in fact shrink and disappear. The system lowers its free energy by some gas leaving the water, but it raises its free energy by creating new interfacial area (the units of surface tension are energy per unit area). On balance the process cannot occur because the net change is an increase of free energy. For the precipitation of solids from a saturated solution, the same analysis applies. In all cases of nucleation, the phase change results in a favorable energy change proportional to volume precipitated or radius cubed, combined with an unfavorable energy change proportional to new area created or radius squared. For small values of radius (nucleation by definition)  $r$  squared is bigger than  $r$  cubed and so the process is unfavorable energetically.

To get gas evolution, we need a "seed" bubble, or nucleation site. This is provided by the walls of the glass. A typical gas nucleation site is a crevice in which there is pre-trapped air or gas. At such a place, the pre-existing liquid/gas interface can have a radius of curvature such that the interface can grow instead of shrink. The result is that the bubble grows out of this feature until it is so big that buoyancy lifts it up and a pinch off occurs. Then the process begins again, with the result being a steady stream of bubbles leaving that nucleation site.

This explains a number of common experiences we have all had. It explains why shaking a can of soda makes it fizz explosively when opened. The shaking puts thousands of small bubbles into the soda. When opened, these nucleation sites allow gas evolution by bubble growth at each site, causing explosive fizzing. A cup of nearly pure water put in a microwave and heated presents an imbalance of gas molecules (steam) wanting to escape and looking for nucleation sites. If the cup is very smooth with few nucleation sites and there are no impurities in the liquid, the gas will be starved for nucleation sites.

When the cup is removed from the microwave and a tea bag is placed in the hot water, an explosive reaction can occur as the enthalpy of the system is allowed to

change rapidly with the addition of huge amounts of nucleation sites. Long ago, chemists invented boiling beads to prevent such dangerous percolation effects in hot beakers of water.

### **Osmosis and Reverse Osmosis**

Gibb's Law of Free Energy also explains the process of Osmosis. Gibb's noticed that particles of pollen when added to water would move in a random pattern. His theory was that nuclei within the bulk liquid were in a constant state of collision and that this random pattern represented a state of equilibrium. This was later proven mathematically by Einstein in 1905.

It turns out that ions in solution exert a pressure on the walls of the container exactly as though they were gas molecules. If two chambers are separated by a reverse osmosis membrane (permeable to water but not ions), with pure water on one side and water plus ions on the other side, there will be a pressure difference between the two chambers according to the relation  $PV=nRT$ . This is the ideal gas law.  $P$  is the osmotic pressure,  $V$  is the volume of each chamber,  $n$  is the number of moles of dissociated ions in each chamber,  $R$  is the universal gas constant and  $T$  is degrees Kelvin. The pure water side has zero osmotic pressure since  $n$  is zero on this side. We know that one mole occupies 22.4 liters at standard temperature of 25 degrees C and one atmosphere. Therefore 1/ 22.4 moles per liter of ions will exert one bar of osmotic pressure on the side with the dissolved electrolyte.

### **Saturation of Soluble Ions during Filtration**

When pressure is applied and reverse osmosis occurs, nearly pure water is forced through the membrane thus changing the equilibrium and consequently the concentration of solutes to solvent. If this process continues until the solute reaches its limit of solubility, precipitation is likely to occur. Once precipitation has begun at appropriate nucleation sites, as more water is removed more product is created from the reagents. This will continue, as the system will attempt to keep the concentration of solutes at or below the solubility limit. If water is removed by filtration, but not in enough quantity to reach the solubility limit of the solutes, no scaling or precipitation will occur. One method used during conventional membrane filtration is recover water from the system to the point where solubility limits are not reached. The second method is to use anti-scalants

that either inhibit the growth of crystals or sequester the reagents and thus reduce the available concentration. Another method is to seed the reagents with overwhelming alternate sources for nucleation and dilute any effect of nucleation near the membrane surface.



## FILTRATION SAMPLES OF WASTEWATER

### Calculating % Recovery & Solubility Limits

Conventional membrane systems have strict guidelines for incoming feed water composition. The reason for this is to minimize the potential problem of scaling or precipitating of slightly soluble ions. Precipitated insoluble materials like mineral scale can foul or blind off crossflow membranes quickly. These must be controlled in order to operate the system properly. Levels of reagents are measured to insure that they will remain soluble during the filtration process. These limits can be exceeded to some degree if antiscalants are used to consume reagents or to inhibit and block growth of scale.

For example:

Well Water is to be treated using membranes for purification. The water contains 30 ppm of dissolved silica ( $\text{SiO}_2$ ). The solubility limit of Silica can be 120 ppm depending on pH and temperature. To figure how much pure water can be extracted through filtration before the solubility limit of silica is reached the following equations can be used:

$$120 \text{ ppm (Ksp)} \div 30 \text{ ppm} = 4$$

The Silica can be volume reduced by a factor of 4 before the solubility limit will be reached.

$$100\% \div 4 = 25\%$$

The liquid volume can be reduced by 75% so that a concentrate volume of 25% is left at which point the solubility limit has been reached. This is also known as a 75% recovery. Since near the solubility limit, there is a metastable region where precipitation can occur prior to the solubility limit if favorable conditions exist some safety factor must be used. Slight variations in temperature, pressure, and pH can shift the point of solubility and cause unexpected scaling. For this reason, conventional membrane systems are not run at the solubility limit, rather they are run at significantly less than that or anti-scalants are used to insure safety factor.

In the example above, with 30 ppm of Silica, safe operation for conventional membrane systems would be at 50% recovery without pretreatment or 75% recovery with antiscalant addition. If the silica content of the raw water was 100 ppm, the water is almost not treatable using conventional membranes alone. Water softening must be used to reduce the hardness and mineral content to sufficiently low levels prior to entry into the membrane system.

It should be mentioned that effective means are available for cleaning of mineral scale and many membrane systems are fitted with Clean in Place (CIP) functions for this purpose. The difficulty is that with rapid or heavy mineral scale formation, membrane cleaning would be frequent and expensive.

### Kinetics of Scaling

**The discussion above concludes that it is thermodynamically impossible to begin the precipitation or crystallization process without a nucleation site.**

Once the process of precipitation has begun it is a separate analysis that is required to get the rate at which precipitation will occur. To grow a crystal, atoms must diffuse toward the interface where they can incorporate into the solid phase. There is therefore a depleted region near the surface of all forming particles which is fed by diffusion from the bulk solution. Antiscalants do their job by interfering with the arrival and incorporation of ions into the particle. These are surface active molecules which absorb to the growing nucleated particles thus getting in the way of the dissolved mineral salts attempting to precipitate. Without antiscalants, the rate is predominantly controlled by the total amount

of liquid-solid interfacial area. The rate is pretty much controlled by diffusion at each individual particle. If the particles are attached to a membrane surface, then one-sided growth may occur because the membrane limits access to the adjacent particle surface. In this case particles may grow as a sheet until they form a contiguous mat of precipitate in the membrane surface. From a fouling perspective this is very undesirable.

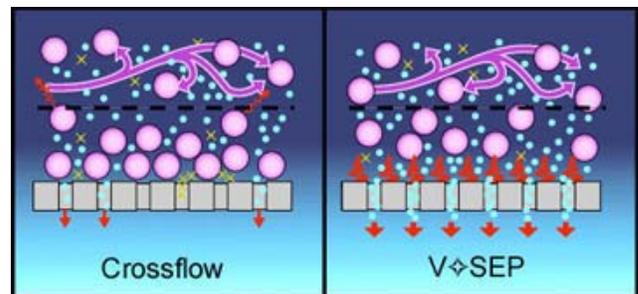
In a functioning membrane system there are simultaneous processes some potentially capable of fouling the membrane surface while others are harmless. Far from the membrane surface, there are nucleation sites in the form of free floating colloidal particles. Perhaps these arrive with the feed material, or maybe they have formed by chemical precipitation. These particles remove the stress of super saturation at a rate proportional to the total surface area of these particles. Meanwhile, at the membrane surface, the stress of super saturation is growing as water is removed, and supersaturated liquid is created at the membrane surface. The concentration is a maximum at the membrane surface, and decays away into the bulk liquid. If there are solid particles available to serve as nucleation sites at the membrane surface these will grow at the fastest rate since they exist at the highest degree of super saturation. If there are no such particles, nucleation is suppressed, and the ions rejected by the membrane will diffuse away into the bulk where they will precipitate on free floating particles. These particles will eventually be convected out with the reject stream and so fouling does not occur. It really matters from a fouling stand point whether the nucleation sites are on the membrane surface, or are in the bulk solution. The nucleation site for commencement can be any perturbation of a surface at a liquid/solid interface. This surface can be a polymeric membrane, suspended solids, system components, etc. Some nucleation sites are more favorable than others, so crystallization and scaling will occur first at the most favorable perturbations with the most amounts of free energy available. While some scaling can occur on a polymeric membrane itself, most membrane surfaces are relatively low energy and are not the best source for crystal formation. Most crystal formation will occur in the bulk of the liquid where plenty of imperfect solid surfaces exist in the form of suspended solids, cake layers of organic matter, metal components, etc. Fouling occurs if the population of nucleation sites at the membrane surface is large in comparison to the number of sites away from the membrane surface.

## Scale Problems & Conventional Membranes

When scaling occurs in a membrane system, colloids of insoluble mineral salts are formed. While some scaling can occur on the membrane itself, most of it will occur at other more efficient locations and then will become suspended colloids, which will act as any other suspended solid during the filtration process. Conventional membranes are subject to colloidal fouling as suspended matter can become polarized at the membrane surface and obstruct filtration. Crossflow is used to reduce the effects of concentration polarization. The main problem with scaling for membrane systems is that the process introduces a large amount of potential foulants into the system, which can reduce flux. Just as conventional membranes have limits on TDS due to the solubility limits of the various constituents, they also have limits on TSS, as colloidal fouling will occur if these levels are too high.

## Scaling Formation in Vibrating Membranes

V $\diamond$ SEP employs torsional oscillation at a rate of 50 Hz at the membrane surface to inhibit diffusion polarization of suspended colloids. This is a very effective method of colloid repulsion as sinusoidal shear waves from the membrane surface help to repel oncoming particles. The result is that suspended solids are held in suspension hovering above the membrane as a parallel layer where they can be washed away by tangential crossflow.



## DYNAMIC FILTRATION

### Fluid Dynamics Comparison Between V $\diamond$ SEP and Conventional Crossflow Filtration

This washing away process occurs at equilibrium. Pressure and filtration rate will determine the thickness and mass of the suspended layer. Particles of suspended colloids will be washed away by crossflow and at the same time new particles will arrive. The removal and arrival rate will be different at first until parody is

reached and the system is at a state of equilibrium with respect to the diffusion layer. (Also known as a boundary layer) This layer is permeable and is not attached to the membrane but is actually suspended above it. In V $\diamond$ SEP, this layer acts as a nucleation site for mineral scaling. Mineral scale that precipitates will act in just the same way as any other arriving colloid. If too many of the scale colloids are formed, more will be removed to maintain the equilibrium of the diffusion layer. As documented by other studies, V $\diamond$ SEP is not limited when it comes to TSS concentrations as conventional membrane systems are. Conventional membrane systems could develop cakes of colloids that would grow large enough to completely blind the conventional membrane. In V $\diamond$ SEP, no matter how many colloids arrive at the membrane surface there are an equal number removed as the diffusion layer is limited in size and cannot grow large enough to blind the system. In fact V $\diamond$ SEP is capable of filtration of any liquid solution as long as it remains a liquid. At a certain point, as water or solvent is removed, the solution will reach a gel point. This is the limitation of V $\diamond$ SEP.

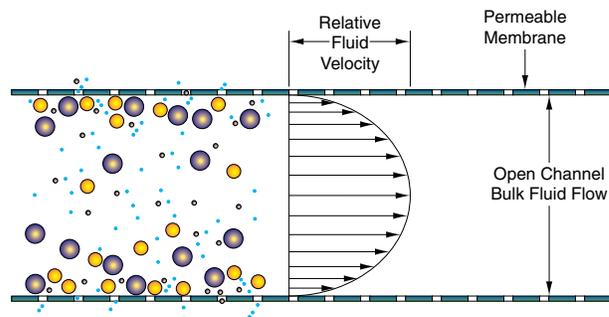
### V $\diamond$ SEP Advantages

In the V $\diamond$ SEP membrane system, scaling will occur in the bulk liquid and become just another suspended colloid. One other significant advantage is that the vibration and oscillation of the membrane surface itself inhibits crystal formation. Just as a stirred pot won't boil, lateral displacement of the membrane helps to lower the available surface energy for nucleation. Free energy is available at perturbations and non-uniform features of liquid/solid interfaces. With the movement of the membrane back and forth at a speed of 50 times per second, any valleys, peaks, ridges, or other micro imperfections become more uniform and less prominent. The smoother and more uniform a surface, the less free energy is available for crystallization.

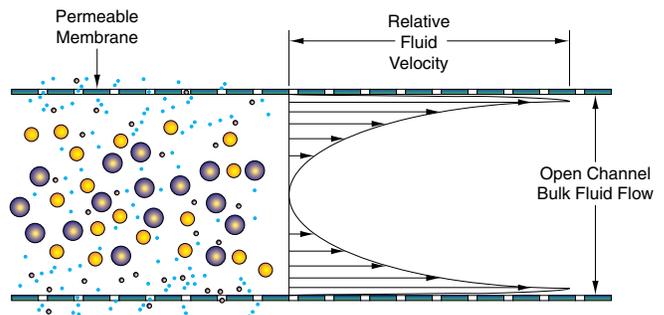
In the absence of any other nucleation sites, this would lead to a super-saturated solution. In actual fact, what happens is that nucleation occurs first and primarily at other nucleation sites not being on the membrane, which present much more favorable conditions for nucleation. Crystals and scale also take time to form. The moving target of the membrane surface does not allow sufficient time for proper germination and development. Other stationary features within V $\diamond$ SEP present a much more favorable nucleation site. Whereas, with conven-

tional membranes that are static, scale formation on the membrane is possible and has plenty of time to develop and grow. Another feature of V $\diamond$ SEP is that filtration occurs at a dramatically higher rate per m<sup>2</sup> than with conventional membranes due to the suspension of colloids above the membrane. Studies have shown as much as a 15x improvement in flux per area. The result of this is that as much as 1/15<sup>th</sup> of the membrane area is required to do the same job as a conventional crossflow membrane. This is beneficial for many reasons one of which is hold up volume of feed waters.

Tangential Flow Pattern in Crossflow Membrane Systems



Tangential Flow Pattern in Vibratory V $\diamond$ SEP Membrane Systems



### LAMINAR FLOW PATTERNS WITHIN CONVENTIONAL CROSSFLOW & V $\diamond$ SEP

The result is that filtration occurs quickly and the length of travel of feed waters over membrane surfaces is reduced by as much as 15x. This means that there is much less time for scaling and crystal formation within the membrane system. Crystal formation is a function of time, especially with respect to Silica, which is very slow to grow. If scaling is to occur within the system, it will more likely occur at high-energy nucleation points and not on the membrane. In addition to that, the high filtration rate is capable of making a super saturated solution, which may not even have residence time sufficient to react within the membrane system itself and may wait until it has been discharge to complete the equilibrium process.

In fact, full scale V $\phi$ SEP membrane systems employing vibrational shear are installed for a colloidal silica gel processing application. The concentrations of silica are way beyond even the point of super saturation and the function of filtration is dewatering of suspended insoluble silica colloids. Other installations include Calcium Carbonate concentration, Titanium Dioxide dewatering, Bentonite Clay clarification, and other precipitated earth metal mineral slurries.

### Validation Testing

A test protocol was developed to test the theories proposed above. In this case, V $\phi$ SEP would be tested with respect to mineral scaling so that the actual results can be used to confirm theory. It is necessary to isolate the variable of mineral scale formation on the membrane itself in a static system and also in a vibrating membrane system for comparison. To test this theory the following protocol was developed.

### Protocol One: Tap Water Concentration

#### Objective

Normal City tap water contains reagents for hardness precipitation. The first study looked at measuring the concentrations of earth metal ions in the water and then concentrating the solution past the point of the solubility of these materials. The objective of this test is to isolate the variable of mineral scale formation and measure its effect on membranes while vibrating. Based on the process objectives given, the following membrane was chosen for study:

#### X-20™\* Reverse Osmosis Membrane

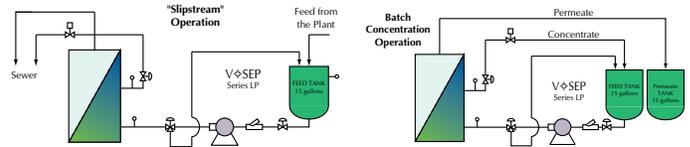
Composition	Polyamide Urea
Nominal Salt Rejection	99.0%
Operating Pressure	0-600 psi
Continuous pH Range	4-11
Max Flat Sheet Temp	60°C

\*X-20 is manufactured by Trisep corporation under license from Dupont

#### Procedure

The V $\phi$ SEP pilot scale Series L unit and feed tank was used for this test with X-20 Polyamide membrane installed. The system is first configured in “Slipstream Mode”. Once the membrane is installed and the machine is configured, the system is first started up running on a continuous feed of DI (deionized) water for

a 100 hour “Line Out Study”.



The data from this is collected for comparison. Then the system is fed with 100 gallons of DI water with NaCl added to simulate the conductivity of normal tap water. The permeate is discharged to drain and the reject is returned to the feed tank for a concentration study in “Batch Mode”. Once this data has been collected, the system is set up with the same feed tank filled with Ultrafiltration permeate of tap water. The unit is started and fed water out of the tank and permeate is sent to drain while reject from the filtration is returned to the feed tank. The tank is volume reduced until 99.98% of the volume is removed as filtrate.

#### Performance

The following Table shows the relative performance of each study

Line Out	Initial Flow	Ending Flow
DI Water	132 ml	92 ml
NaCl + DI Water 99% Rec	125 ml	75 ml
UF Permeate 99.98% Rec	128 ml	72 ml

\* Flow Rates are ml/min corrected to 25°C

Table 1: Tap Water Sample Analysis

Description	Silica	Calcium	Magnesium	Barium
RO Feed Water	5.3 ppm	24 ppm	5.5 ppm	<1 ppm
RO Permeate	<1 ppm	2 ppm	<1 ppm	ND
RO Concentrate	26,200 ppm	110,000 ppm	27,400 ppm	1,130 ppm
Solubility Limit	120 ppm	180 ppm	42 ppm	10 ppm

\*TC 25°C, pH 7.0, 400 psi



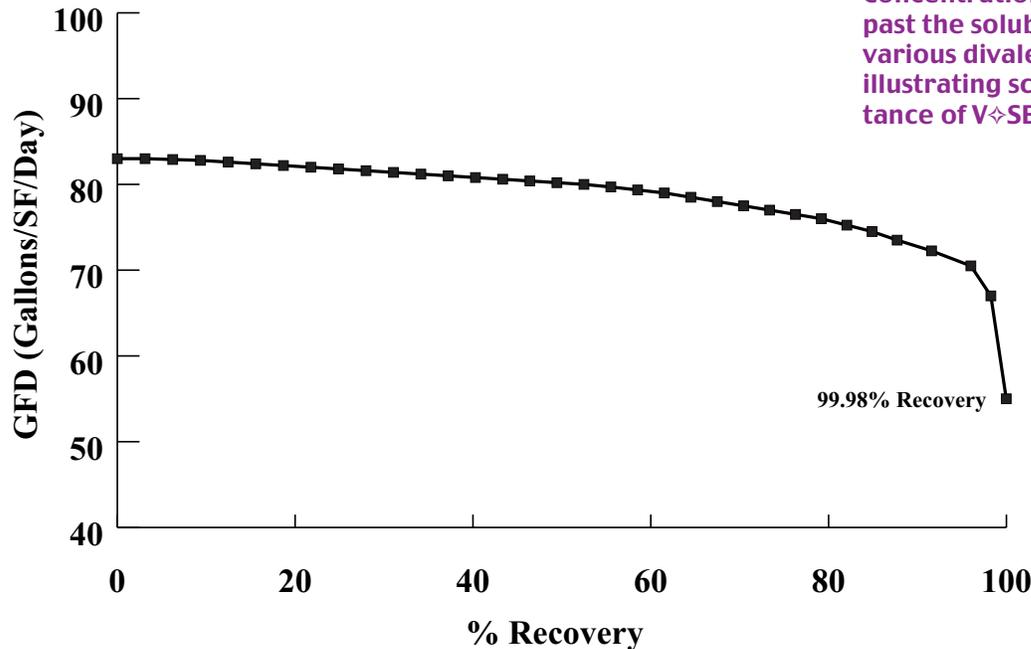
SAMPLES OF TAP WATER

## RO Concentration of Municipal Tap Water

Using VSEP (Vibratory Shear Enhanced Process)  
Test Conditions: 400 psi, 25°C, City of Oakland Tap Water

### GRAPH ONE

Flux vs % Recovery  
Concentration of Tap Water  
past the solubility limits of  
various divalent metals  
illustrating scaling resis-  
tance of VSEP



The objective is to isolate the effects of solubility of various reagents as much as possible. Many variables can affect permeate flow rates over time. Here the DI water test was used to measure what effect 100 hours of 450-psi pressure would have on the membrane. The concentration of saline DI water can be used to measure the effects of polarization of ionic species. The final line out study uses UF permeate of tap water where suspended solids colloids, and organic materials are removed by the UF process so that the remaining solution contains only dissolved and disassociated ions and water. The final line out adds the effect of solubility limits being reached and surpassed. The effects of time and pressure and the effects of ionic polarization can be measured. The final line out includes these two variables as well as mineral precipitation. If the first two variables are subtracted from the final results, it is assumed the remaining measured effect is nearly entirely due to mineral scale formation.

### Results

The data series represents the final UF permeate concentration with the effects of ionic polarization and pressure effects being removed according to the data in the first two line outs. This final data series shows the isolated effect of filtration past the solubility limits of mineral reagents in tap water.

### Protocol Two - Super-Saturated Silica Filtration

#### Objective

The first test measured performance on the various minerals found in tap water as they reach their solubility limit. This test was done to measure performance of vibrating membranes while dewatering a super-saturated solution of dissolved silica. The objective is to isolate silica precipitation alone and measure the effect on filtration rates.

#### Procedure

The VSEP pilot scale Series L unit and feed tank was used for this test with X-20 Polyamide membrane installed. The system is first configured in "Batch Mode". A solution of super-saturated dissolved silica is prepared by first dissolving Silicon metal fines in a ten-gallon solution of pH10 RO Permeate water. The concentrated solution of dissolved Silica is added to the feed tank and pH adjusted to 7.0 using HCl. At this reduced pH, the solubility limit has been surpassed and the solution is super-saturated. Once the membrane is installed and the machine is configured, the system is first started up running on a continuous feed of saturated Silica for a 150 hour "Line Out Study". The data

from this is collected for comparison. Then the permeate is discharged to drain until 5 gallons of water have been removed. Once this data has been collected, the system is run for a long-term line out study.

Performance

The following Table shows the performance of the study during the “Line Out” & “Concentration” period

<b>Procedure:</b>	<b>Initial Flow</b>	<b>Ending Flow</b>
<b>Saturated Silica Line Out</b>	132 ml	105 ml
<b>Silica Concentration</b>	128 ml	85 ml

\* Flow Rates are ml/min corrected to 25°C

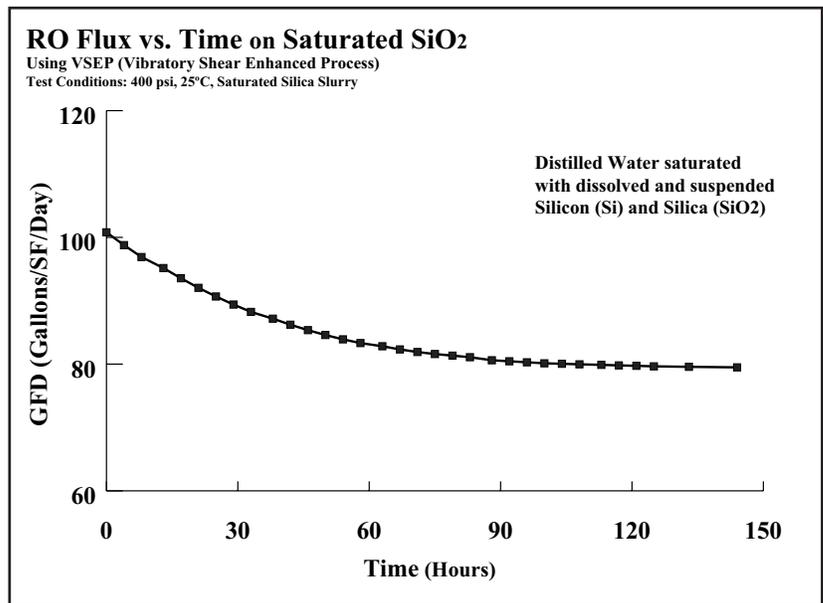
Results

The results of the line out and concentration are shown graphically. The first data series shows the effects of flux vs time as the boundary layer of colloidal suspended solids forms over the membrane and finally reaches equilibrium. The second data series shows primarily the results of ionic polarization as the feed water is concentrated. No sign of significant Silica wetting or scaling is apparent.

**Table 2: Saturated Silicon/Silica Sample Analysis**

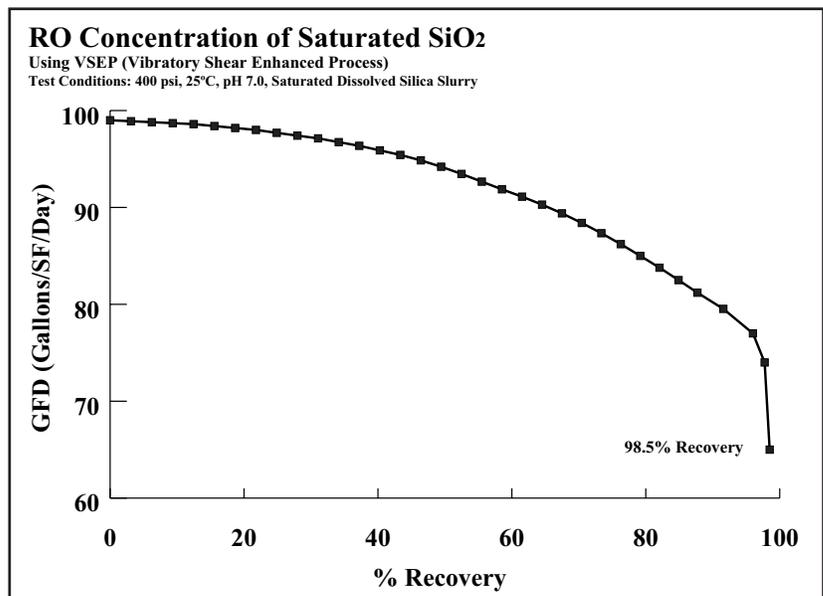
Description	Amount
RO Feed Water Total Silica Concentration	620 ppm
RO Permeate Total Silica Concentration	42 ppm
RO Concentrate Total Silica Concentration	31,900 ppm
Total Permeate Recovery	98.5 %

\*TC 25°C, pH 7.0, 400 psi



**GRAPH TWO (ABOVE RIGHT)**  
**Flux vs % Time**  
**Filtration of Saturated Silica Line out**

**GRAPH THREE (RIGHT)**  
**Flux vs % Recovery**  
**Concentration of Saturated Silica**



### Protocol 3 - Saturated Calcium Sulfate Filtration

#### Objective

Since Silica scale forms by wetting surfaces and tap water contains a composite amount of scalants, another test was conducted to isolate one specific crystallizing mineral scalant. The objective of this test was to isolate Calcium Sulfate (Gypsum) precipitation alone and measure the effect on filtration rates.

#### Procedure

A pH 3 solution of super-saturated dissolved  $\text{CaSO}_4$  is prepared by first dissolving in water and then filtering using a UF membrane. The UF membrane is used to removed any suspended solids and leave behind dissolved Calcium in the presence of Sulfates. The concentrated solution of dissolved Calcium Sulfate is added to the feed tank and pH adjusted to 8.0 using HCl. At this pH, the solubility limit has been surpassed and the solution is super-saturated. The solution is filter using an X-20 RO membrane and concentrated by removing permeate from the feed tank until 98.5% of the water has been taken out.

#### Performance

The following Table shows the performance of the study during the “Line Out” period

<b>Procedure:</b>	<b>Initial Flow</b>	<b>Ending Flow</b>
<b>Gypsum Concentration</b>	94 ml	70 ml

\* Flow Rates are ml/min corrected to 25°C

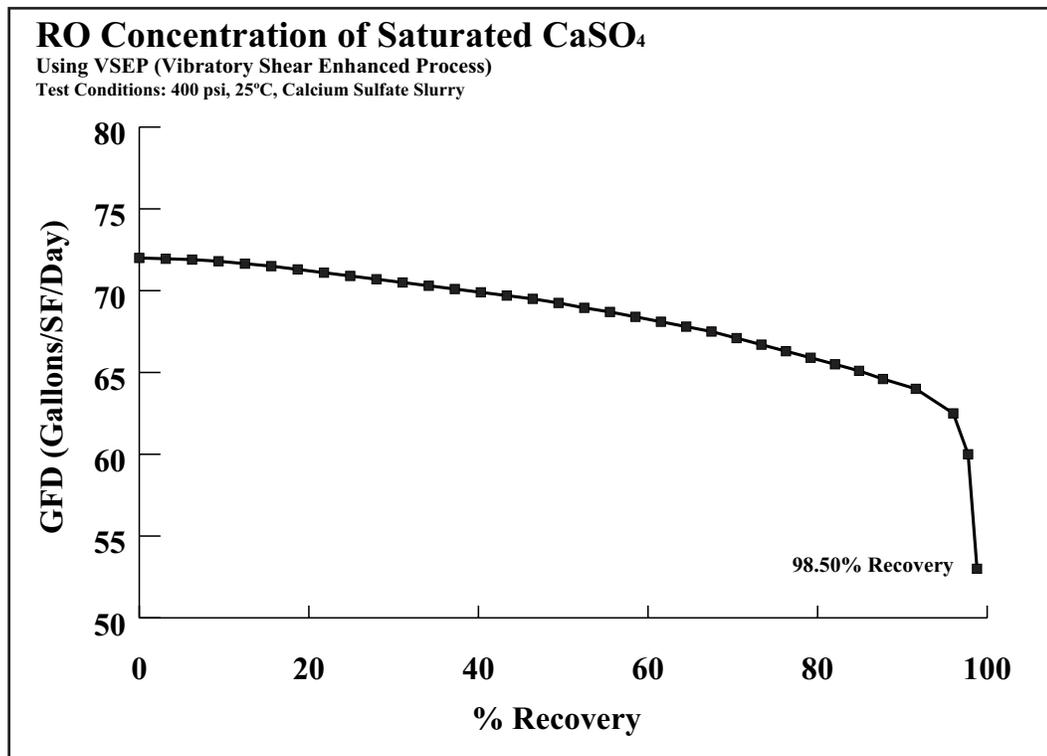
#### Results

The results of the data series shows primarily the results of colloidal polarization as the feed water is concentrated. No sign of significant mineral scaling is apparent.

**Table 1: Saturated Calcium Sulfate Sample Analysis**

Description	Amount
RO Feed Water Calcium Concentration	1420 ppm
RO Permeate Calcium Concentration	30 ppm
RO Concentrate Calcium Concentration	92,600 ppm
Total Permeate Recovery	98.5 %

\*TC 25°C, pH 8.0, 400 psi



**GRAPH FOUR**

**Flux vs % Recovery**

**Concentration of Calcium Sulfate past the solubility limit**

## Protocol Four - Vibration Study

### Objective

The above tests were able to measure the effects of filtration past the solubility limits of various dissolved species, another test was conducted to try the same thing using a static non-vibrating membrane that would simulate a conventional crossflow system. A simple Line out study is done to measure the effects of filtration of a saturated Calcium Sulfate solution with and without vibration.

### Performance

The following Table shows the performance of the study during the "Line Out" period

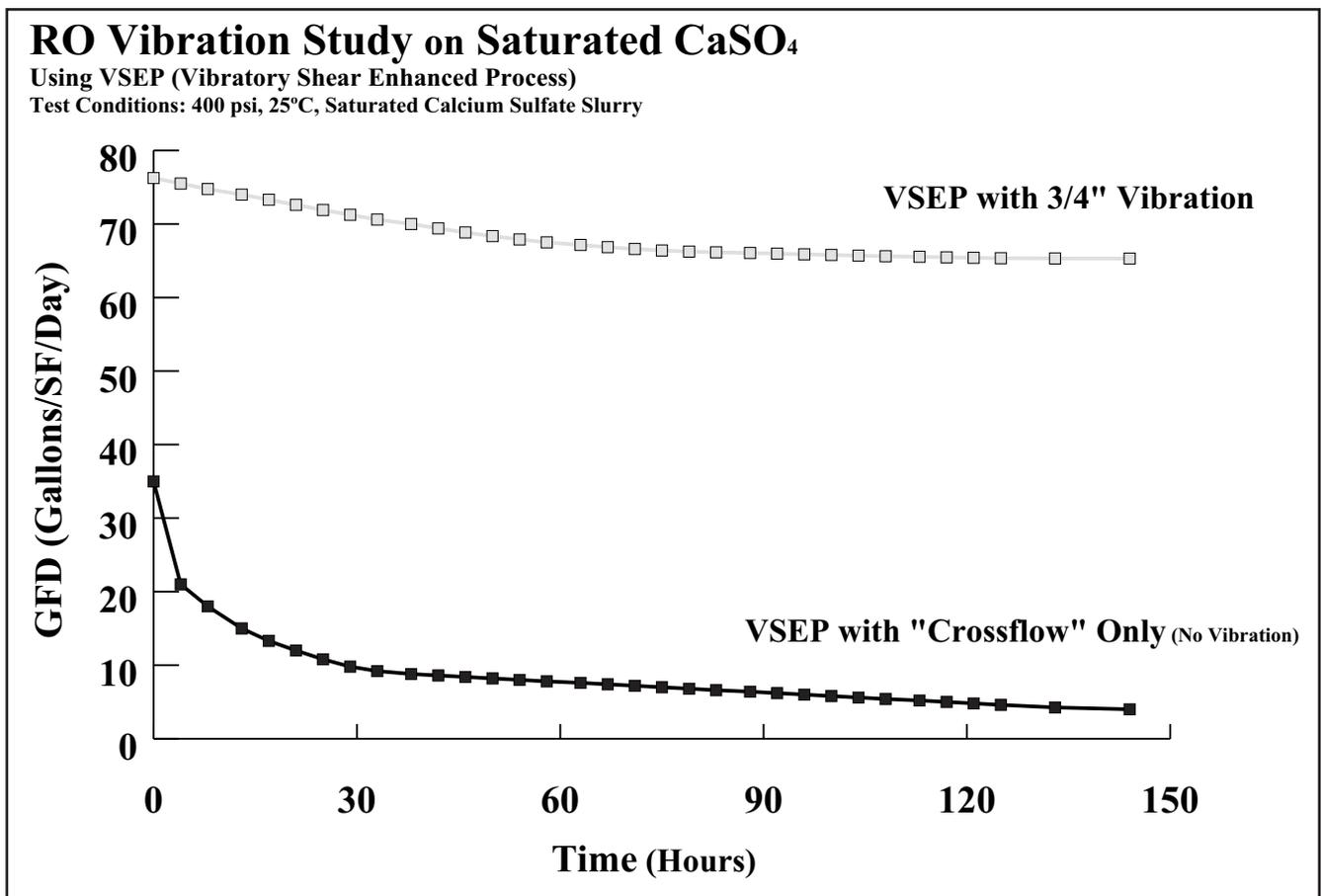
Procedure:	Initial Flow	Ending Flow
Filtration with Vibration	100 ml	86 ml
Filtration without Vibration	46 ml	9 ml

\* Flow Rates are ml/min corrected to 25°C

### Results

This test run with and without vibration from the same feed material under the same operating conditions illustrates the benefits of vibration during filtration of saturated hard water. In this case, the line out with vibration represents about a 9x increase in flux.

The flux decline in the vibration data series reveals the formation of the boundary layer of hovering solids and it can be seen where this layer reaches equilibrium. The no vibration data series starts with a relatively high rate of flux and then drops quickly as fouling and scaling start to occur.



GRAPH FIVE

Flux vs % Time  
Filtration of Calcium Sulfate with Vibratory Shear and without vibration and crossflow only.

## **Conclusion**

Other studies have shown that vibration can reduce the effects of concentration polarization while using UF membranes, this study illustrates the effects are the same for RO membranes. Mineral scaling, predominant in conventional membrane systems, which is caused by the deposition of colloidal materials in close proximity to the membrane surface and leading to fouling can be held off the membrane by vibrational shear found in systems like VSEP. Once mineral salts evolve, they would act as any other suspended colloids in the vibrational membrane system. VSEP is uniquely capable of reducing the effects of colloidal fouling including precipitated mineral scales that can form. The study also illustrates that nucleation and crystal formation occurs in the system, but, is not able to form in significant quantities on the vibrating membrane surface itself, and rather, forms in the bulk of the media at other more attractive nucleation sites with more available free energy.

## **References**

- [1] Douglas M Ruthven, Separation Technology, Wiley-Interscience 1997
- [2] J. Mallevalle, I.H. Suffet, U. S. Chan, Influence and Removal of Organics in Drinking Water, Lewis Publishers 1992
- [3] Milton J. Rosen, Surfactants and Interfacial Phenomena, Second Edition, Wiley Publications, 1898
- [4] I. Bremere, M. Kennedy, P Michel, R. Emmerick, G. Witkamp, J. Schippers, Desalination (1999) 51-62
- [5] R. J. Bowell, Sulfate and Salt Minerals, Mining Environmental Management May 2000
- [6] R. Brian, K. Yammamoto, Y. Watanabe, Desalination Publications, ISBN 0-86689-060-2, Oct 2000