CASE STUDY

Frac Water and Flowback

VSEP membrane treatment on site for water reuse

Background

Conventional oil and gas wells are drilled into geological formations that are very porous and once the cap is penetrated, the oil and gas are removed easily. Sometimes as the well becomes depleted, water flooding or steam flooding is used to help push the oil out of the formation.

Oil and gas are found in many more areas where the extraction is not so easy. New horizontal drilling techniques and other modern technology advancements have allowed this energy source to be accessed more easily. “Unconventional” oil and gas formations can be found in shale and coal deposits where the geological formation is very tight and not porous. Shale is very densely packed, but can contain large amounts of natural gas.

After well hole is drilled into these shale formations, casings are installed to isolate the wellbore. The bottom section of this casing is perforated so that gas can more easily be removed. Once the casing is in place in addition to concrete reinforcing in the upper sections, water and sand are injected under high pressure into the shale deposit. This creates small fractures in the shale and provides openings making the formation porous for gas removal. When the water pressure is relieved, the small cracks in the shale begin to close, but the sand or ceramic particles help to “prop’ them open. These materials are known as “Proppants”. In addition to the water and the sand, small amounts of various chemicals are added for various purposes. These include biocides, surfactants, corrosion inhibitors, thickeners, and other materials.

This water that is used to fracture the shale formation is called “frac water”. The process of fracturing is also known as completion since this is one of the final steps in preparing a well for production of oil or gas. Frac water can also be known as “completion fluid”. When the pressure of this water is relieved, the water flows back up out of the well casing. This is known as “Flowback water”. Some of the water will remain down in the hole and be absorbed into the more porous areas. The amount of water that flows back can vary a great deal and can be anywhere from 10% to 90% of the water that is injected as frac water.

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The Flowback water can be reused to some extent, but as the water is injected into the shale formation, it absorbs minerals, salts, organics, and also brings sediment back out with it when it flows back. At a certain point, this water becomes too “dirty” to reuse. The conventional thing to do at that point is to haul this water off by truck for disposal. Many well sites are in remote areas and do not have established connections to municipal; sewers or to disposal wells for reinjection. This hauling can involve a high cost and the use of many trucks that can put a burden on the local community.

Some Potassium salts are added to the frac water to begin with. Some salt in the frac water is desired, but very high levels of mineral salts that can cause scaling and plugging of the formation would adversely affect the operation. Also injecting frac water that has a lot of sediment can also plug the formation. So before the Flowback water is reused, sediment and other fouling materials should be removed. Onsite water treatment can provide almost unlimited reuse of the Flowback water and greatly reduce the need for truck hauling. In addition to the benefits of less hauling, many locations have scarce supplies of fresh water that is available for use as frac water. So, reuse of the Flowback water can reduce the amount of local fresh water that is consumed as well as reuse the amount of wastewater hauled away.

These two benefits will vary in importance from region to region. In Texas, good ground water is in very short supply and fresh water availability is much more of a problem than disposal of the wastewater since there are many disposal wells in Texas that are located near the frac site. However, in Pennsylvania, there is more fresh water available, but no injection wells and the wastewater will need to be hauled for many miles, sometimes to other states.

VSEP Treatment of Flowback Water

New Logic has worked with many water treatment companies who provide mobile Flowback water treatment over the last 10 years. There have been many scenarios used, but in all cases, a mobile VSEP membrane water treatment system manufactured by New Logic is used to recycle the water and minimize the waste that is generated.

Studies conducted on the Flowback water show a very wide range of total dissolved solids (TDS) concentrations in the water. Levels from 4,000 to 150,000 mg/L have been observed. This wide range can make treatment difficult and the choice of the right membrane or treatment scenario will depend on the makeu p of the Flowback water.

Preliminary studies should be conducted to determine what the Flowback water would look like, and then a treatment option can be designed. Higher TDS levels will reduce the throughput rate of the VSEP membrane module when NF or RO membranes are used, so more membrane modules would be needed for a given flow rate capacity.

VSEP Treatment Process

VSEP (Vibratory Shear Enhanced Process) employs torsional vibration of the membrane surface, which creates high shear energy at the surface of the membrane. The result is that colloidal fouling and polarization of the membrane due to concentration of rejected materials are greatly reduced. Since colloidal fouling is avoided due to the vibration, the use of pretreatment to prevent scale formation is not required. In addition, the throughput rates of VSEP are 5-15 times higher in terms of GFD (gallons per square foot per day) when compared to other types of membrane systems. The sinusoidal shear waves propagating from the membrane surface act to hold suspended particles above the membrane surface allowing free transport of the liquid media through the membrane.

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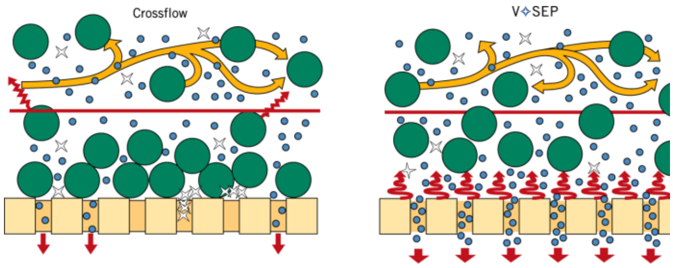

The VSEP membrane system is a vertical plate and frame type of construction where membrane leafs are stacked by the hundreds on top of each other. The result of this is that the horizontal footprint of the unit is very small. As much as 1400 square feet (140 m2) of membrane is contained in one VSEP module with a footprint of only 4' x 4'.

VSEP 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 gentle tangential crossflow.

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 parity 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 VSEP, this layer acts as a nucleation site for mineral scaling. Beneath the hovering suspended solids, water has clear access to the membrane surface.

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, VSEP 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 VSEP, 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 VSEP 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 concentration limitation of VSEP.

In the VSEP 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. The 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.

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Since VSEP is not limited by solubility of minerals or by the presence of suspended colloids, it can actually be used as a crystallizer or brine concentrator and is capable of very high recoveries of filtrate. The only limitation faced by VSEP is the osmotic pressure once dissolved ions reach very high levels. Osmotic pressure is what will determine the recovery possible with a VSEP system.

Membrane Introduction

VSEP uses polymeric membranes which are thin filter cloths with a porous plastic top layer. New Logic has over 200 membranes of various types and sizes that it uses depending on the separation that is required. There are four main categories of membrane filtration. These are determined by the pore size or molecular weight cutoff:

Filtration Type	Particle Size Rejection	Molecular Weight cutoff
Reverse Osmosis	≤ 0.001 µm	≤ 100 Daltons
Nanofiltration	0.001 - 0.01 µm	100 - 1000 Daltons
Ultrafiltration	0.01 - 0.1 µm	1000 - 500,000 Daltons
Microfiltration	≥ 0.1 µm	≥ 500,000 Daltons

Reverse Osmosis Membranes

The first category of membranes is Reverse Osmosis (RO). These are the tightest membranes for separating materials. They are generally rated based on the amount of sodium chloride that they can remove from a feed stream. Usually, the rejection of NaCl will be greater than 95% for a membrane to be classified as an RO membrane. An example of their use would be for filtering seawater to remove the salt. They are also used to remove color, fragrance and flavor from water streams. RO will remove all types of solids whether they are dissolved or suspended.

Nanofiltration Membranes

A great deal of recent research has led to the improvement of membranes in the range of Nanofiltration (NF). As the name suggests, these membranes are used to separate materials on the order of nanometers. These membranes are not usually rated based on their pore size because the pores are very small and difficult to measure accurately. Instead, they are rated based on the approximate molecular weight of the components that they reject or the % of sodium chloride that they can remove from a stream. These membranes can remove all suspended solids, free oil, bacteria, and viruses. NF will remove the majority of multi-valent ions such as Calcium and Iron. NF will also remove color and BOD. However, monovalent ions such as Sodium and Potassium will not be rejected very much.

Ultrafiltration Membranes

Conventional Ultrafiltration (UF) membranes are composed of some type of polymer material with pore openings ranging from a little less than 0.01 µm to 0.1 µm. These membranes are used for many different separations including: oily wastewater treatment, protein concentration, colloidal silica concentration and for the treatment of various wastewaters in the pulp & paper industry. UF membranes can remove suspended solids, free oil, and large organic molecules.

Microfiltration Membranes

These membranes tend to be porous, with pores greater than 0.1µm. These types of membranes are used to separate larger particulate matter from a liquid phase. Some examples would be coarse minerals or paint particles that need to be concentrated from an aqueous solution.

Membranes are usually made up of two parts: a discriminating surface layer and a backing material for support & strength. The filtering surface layer can be made from many types of polymers, some natural and some synthetic. The type of polymer, method of casting onto the backing, and whether it is stretched determine the size of the pore structure in the membrane layer. New Logic staff will assist you in the proper membrane selection.

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Membrane Choices for Flowback Water

A mobile VSEP system with a RO membrane can be used as a single step for solids removal and desalination if the TDS level is 25,000 mg/L or less. In a single step VSEP would produce concentrate brine and also clean water for reuse.

However, most Flowback water has TDS higher than this. With higher TDS, higher pressure is needed to generate filtrate from an RO membrane. If the Flowback water TDS is between 25,000 and 100,000, the best scenario is to use a VSEP system with a looser membrane first and then use a spiral RO membrane system at high pressure for desalination. If the TDS is too high, then VSEP can be used as pretreatment to distillation, crystallization, or evaporation. RO membranes would probably not be practical due to the extremely high osmotic pressure in these cases. The VSEP systems are adaptable and since each well site water will be different, the overall treatment system will need to be adjusted to fit the conditions.

When the Flowback water is reused, materials in the water that would foul the formation need to be removed first. RO filtrate will be good enough to make water for reuse. If RO can be used as described above, then a solution is available. Nanofiltration is a category of membrane that is regarded as a loose RO. NF will remove all of the suspended solids much of the multivalent sparingly soluble mineral salts that could become saturated and foul the formation, but not in all cases. It is possible that NF by itself would work, but this should be tested to see if the separation is sufficient. NF membranes will flux higher than RO and will not be as affected by osmotic pressure, so NF can be used in very high TDS situations.

Regarding the NF and this feed water, the problem is that the only anion available is often Chloride. Chloride passes pretty easy through a NF membrane because it is monovalent. Because of a principle known as “Donnan Equilibrium”, there must be charge neutrality on both sides of the membrane. If Chloride passes, it will drag a reluctant Cation with it to maintain charge neutrality. Normally a NF membrane will have pretty good divalent rejection, but that would be if both the cation and anion were divalent or multivalent. The results you get with NF on Flowback water show some good reduction, but perhaps not good enough. Barium, Strontium, and Calcium levels are reduced but not as much as they would have been if the Chloride weren’t present.

If NF by itself cannot produce filtered water that is clean enough, then a RO spiral polishing stage or distillation will be needed for desalination. NF will make a very good feedwater for a RO spiral system. It will reduce the TDS level some which reduces the osmotic pressure to the RO. NF will also remove materials that can scale the RO spiral system.

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NF might not be needed though and a more open membrane such as UF or MF could be considered. UF and MF membranes have physical pores and will remove almost 100% of the suspended solids, free oil, and bacteria, but they will not remove dissolved solids. If there are no dissolved solids present in the water that would cause problems for a RO spiral system, then UF or MF can be used to pre-filter for the RO and remove the materials that would plug the RO. UF or MF will flux at a higher rate than NF and so, this options would be less expensive.

So, there are four choices for the kind of membrane to be used for the Flowback water. MF, UF, NF, or RO can be used. The choice of which one to use will depend on the conditions of the water that is to be treated.

Membrane Comparisons

The table below shows the relative performance of each kind of membrane when treating Flowback water. The numbers shown are average and the actual values can very a great deal depending on the makeup of the water treated. But, this table is shown to give you an idea about the relative performance. The use of RO shown in the table would be for cases where the TDS is low enough to allow its use.

	RO – Reverse Osmosis	NF - Nanofiltration	UF/MF - Ultrafiltration
Filter Throughput*	5-14 gpm	6-18 gpm	15-40 gpm
Water Recovered	70%	80%	90%
TSS Reduction	100%	100%	100%
TDS Reduction	90%	20%	0%
Barium Reduction	95%	50%	5%
Strontium Reduction	95%	50%	5%
Calcium Reduction	95%	50%	10%

*for each 84" VSEP module. These can be used in parallel for any flow rate needed.

Nanofiltration Treated Water Quality for Re-use

New Logic has provided mobile VSEP NF system to treat frac water. The nanofiltration permeate is a very clear water and in this case was excellent quality for re-use. The well service company conducted studies on the permeate and described the re-use water as follows:

Conductivity = 29,000 µS
Microbiological content is low
Langelier Saturation Index = 1.15
Calcium Sulfate Scaling Potential is negative
Iron = 0 mg/L
Calcium = 500 mg/L
Magnesium = 15mg/L
Total Hardness = 1,200 mg/L
Sulfate = 0 mg/L
Chloride = 10,000 mg/L
M Alkalinity = 125 mg/L

Pretreatment Chemical Addition options with NF

Another way to make a NF membrane work is to add chemicals to the feed that will drop out some of the Barium, Strontium, and other scaling materials so they can be removed as suspended solids. If soluble, NF will remove about half of these materials with Chloride present. If insoluble, NF will remove 100% of them even with Chloride there. The solution is the make the Strontium or Barium either insoluble, or to pair them up with divalent anions like sulfate so they can more easily be removed with NF.

This should always be tested instead of assumed, but this is an option to be able to use NF and not have to add a desalination step. A chemical is added to convert the divalent Barium or Strontium to insoluble materials, or it will provide a soluble divalent anion that will preferentially associate with the divalent cation. This way the mineral salts are rejected by the NF membrane at a much higher rate since the chloride can now choose another cation such as Sodium or Potassium to maintain charge neutrality in the filtrate.

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Hydroxide salts of Group II metals like Calcium and Strontium and slightly soluble, meaning mostly insoluble. NaOH (caustic soda) can be added as a source of Sodium to pair with the Chloride and Hydroxide to pair with the minerals. This will raise the pH some. In theory, the Na (sodium) would preferentially go to (associate with) the chloride and exchange the sodium for a strontium or calcium. In theory, as you add NaOH, you would drop out Calcium Hydroxide and Strontium Hydroxide. The ratio of OH to any of these metals is 2:1. In other words, if you have 4000 mg/L of Calcium, you need to add 8000 mg/L Hydroxide. Barium Hydroxide is soluble and cannot be remove this way.

Carbonate salts of Group II metals are insoluble. You can add NaCO3 (Sodium Carbonate). The same exchange process will occur and you will get more Sodium Chloride and precipitated Group II Carbonates that can easily be settled or rejected by a NF membrane. (Or UF for that matter).

With Sulfate salts, Strontium, Barium, and Calcium are insoluble. NaSO4 (Sodium Sulfate) could be added to drop these out. Barium Fluoride, Strontium Fluoride, Calcium Fluoride, Barium Chromate, and Calcium Phosphate are also insoluble. Oxides of the three are all different. Barium Oxide is soluble, Calcium Oxide is slightly soluble, and Strontium Oxide is insoluble

So in summary:

- Hydroxides and Oxides can get Calcium and Strontium
- NaCO3, NaSO4, NaF and NaPO4, will get all three including Barium.

The only question is the thermodynamics, or how strong the preferential attraction will be. While Barium Oxide and Barium Hydroxide might still be soluble, they may also have greater charge and could possibly be rejected better by the NF than the Chloride version. Another option not involving chemical addition is to use ion exchange after NF filtration to remove remaining hardness. If chemical treatment prior to NF doesn't make water free enough from scaling minerals, it would improve the performance of a spiral RO polishing system used as a second stage.

While this NF filtrate could be free from materials that would present fouling or plugging issues for the formation, the filtrate will have high levels of other soluble salts. The presence of these may affect the performance of some of the corrosion inhibitors and other additives to the franc water. So, the quality of the NF filtrate would need to be reviewed to see if it is suitable. Using VSEP as pretreatment to RO Spiral will make water that is free of everything including these salts, so there would be no issue with its reuse.

Pretreatment sand removal options

Prior to membrane filtration with VSEP, there could be some pre-treatment steps that would be beneficial. First if there are very large suspended solids, it is best to remove them to reduce risk of damage to the pumps, valves, and to the membrane. Sand and other large solids should be removed. Sometimes, just gravity sedimentation is a lined storage pond will work to drop out these materials. However, this would depend on the conditions at the well site. Each well site location may have different water and different conditions, so the best water treatment system configuration will need to be adapted to fit the conditions.

In cases where there are very fine sand particles that don't settle, then a mechanical filtration step will be needed. Options for this include a vibrating wire mesh screen filter, centrifugation, belt press, etc. Generally, it is best if particles that are 100 mesh (150 micron) or larger are removed prior to filtration with the VSEP system.

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Desalination options

After the fouling materials have been removed with MF, UF, or NF, salt concentrations in the water may need to be reduced. The best system for this work will depend on the dissolved solids concentration. If the TDS level in the pre- treated water is 50,000 mg/L or less, then a high pressure spiral RO system can be used after the VSEP to polish the VSEP filtrate making very clean water for reuse in fracturing. If the TDS were higher than that, then distillation would be an option for water reuse. Distillation equipment can be large and may not be appropriate for mobile transport, so an offsite fixed location would be best. This facility could be located near to the well site and would allow for short haul trips for both the brine water leaving and the fresh water returning. The problem would be finding a property zoned for this kind of activity and also in managing the truck traffic to avoid disturbances.

Onsite desalination is ideal due to the reduced cost, so a 2nd stage RO spiral system would be ideal as long as the TDS level is low enough. These RO spiral systems are easily truck mounted and don’t require a lot of space.

VSEP Systems Components

Each VSEP system is automated with computer controls. The VSEP membrane module itself is vertical and is mounted onto the vibratory base unit. Each of these takes up a space of about 4 ft. x 4 ft. and weighs about 2 tons. The height of the installed module is about 16’, but the filter module can be removed for transportation. Alongside the VSEP module, a control skid is used and has the pumps, piping interfaces, instrumentation, valves, and other controls needed for automated operation. A cleaning tank is included as well. VSEP membranes resist fouling but do need to be chemically cleaned periodically. If a polishing spiral RO system is used, this would be provided as a separate skid. The whole process has a relatively small footprint that can be easily mounted onto a truck trailer.

When the VSEP system is being mobilized and moved onsite, the filter module is not installed during transportation. Once the equipment has arrived onsite, the filter module is installed onto the vibratory based by using a crane or hoist. This equipment could be built into the trailer, or a separate truck can be provided for this activity. When it is time to demobilize, the filter pack is removed again for transportation. This process takes about 2-3 hours.

For more information about a VSEP system, contact Syngineering Water.