

# Water Injection and Sulfate Removal in the Offshore Oil & Gas Industry

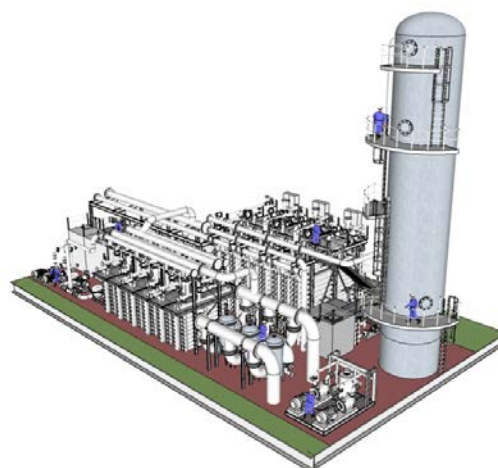
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## Introduction

The Offshore Oil & Gas industry is shifting Exploration & Production efforts towards deeper waters with a significant number of projects located off the coast of Brazil and the coast of West Africa. Some projects are located at depths of more than 2,000m and distances that exceed 300 km from the shore. Wells that are drilled in this environment represent significant logistical and technological challenges stemming from the complexity of drilling thousands of meters in ultra-deep waters. The cost associated with drilling a well ranges from \$100 - \$300 million dollars whereas the cost of an FPSO exceeds the billion dollar mark. This increasing capital intensity translates to a financial risk that Oil & Gas Operators address by protecting their production assets, including subsea infrastructure and wells, in order to maximize their return on investment.

Sulfate Removal is an important part of ensuring that injection and production wells remain free of barium and strontium scale, which would otherwise precipitate if untreated seawater was injected. Removing sulfate from seawater prevents scale buildup in the well and reservoir, increases productivity by preventing pipe constriction due to scale, prevents reservoir souring, reduces equipment corrosion and assists in maintaining reservoir permeability.

The most common way to remove sulfate from seawater is with nanofiltration membrane technology, which is at the heart of the sulfate removal process. Nanofiltration membranes were first commercialized in 1984, introduced for separating diva-



lent ions from monovalent ions in water solutions. This caught the interest of Marathon Oil, which used seawater to drive oil in offshore formations containing high concentrations of divalent cations as calcium, barium and strontium in connate waters associated with oil. Conventional treatment of this problem required the use of high doses of antiscalants and other chemicals making it labor intensive, economically inefficient, technically difficult to control, and environmentally harsh.

Thirty years later, there are over 80 sulfate removal units installed globally, with 5-10 new sulfate removal projects being awarded every year.

## Nanofiltration Membrane for Sulfate Removal

What constitutes nanofiltration or an NF membrane has not been well defined. Many define an NF membrane as any RO membrane that does not give as high salt rejecting as the present state of the art. At GE, we define an NF membrane as a membrane that has a sodium chloride permeability that is proportional to the sodium chloride con-



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centration to a power greater than 0.4. Such membranes reject less than 50% of sodium and chloride when operating on seawater (Eriksson et al. 2005).

Nanofiltration membranes have a pore size around 1.0 nm, which is slightly larger than that of RO membranes and smaller than ultrafiltration (UF) membranes. Separation by nanofiltration occurs primarily due to size exclusion and electrostatic interactions. For uncharged molecules, sieving or size exclusion in NF membrane pore structure is most responsible for separation; for ionic species, both sieving and electrostatic interactions are responsible for separation. For all applications, membrane surface and pore walls charge characteristics play a key role in the transport of water and solute molecules through the membrane. The charge of the NF membrane is dependent on the pH because functional groups of the membrane protonate and deprotonate over the pH range. This in turn affects the membrane rejection performance, because the charge influences the electrostatic repulsion between the ions or charged molecules and the membrane surface. In addition, because of dissociation of membrane functional groups, the pH of the system may affect the “openness” of the membrane. This affects the size exclusion mechanism of removal for NF membrane. Finally, the interaction of colloids in solution with the membrane and subsequent fouling of the membrane are also dependent on the surface zeta potential and pore charge properties (Childress et al. 2000).

Relating this information to seawater, the highly charged surface of the NF Membrane leads to a significant rejection of divalent ions like sulfate, magnesium or calcium. This surface charge however is not high enough to reject the less charged monovalent ions like sodium and chloride. In general, the higher the ionic strength of seawater, the lower is the rejection of monovalent ions. Non-charged molecules with greater than 1 nm in size are practically completely rejected.

The tendency of NF membranes to foul during operation is influenced to a great extent by surface roughness. Typical average and root mean squared surface roughness of commercial RO membranes as measured using tapping mode atomic force microscopy (AFM) have been variously reported in the range 30–100 nm (Yang et al. 2009, Hurwitz et al. 2010). In contrast, surface roughness of the GE’s sulfate reducing NF membrane is much lower, typically 10 nm or less. Bowen et al. (2002) confirm the

smoother surface of GE’s membrane compared to that of RO membranes. Lower surface roughness is a desirable property in a sulfate removal water injection application as it leads to decreased fouling, which in turn has an impact on membrane performance, chemical cleaning requirements and membrane longevity.

## GE’s Sulfate Reducing NF Membrane

GE’s Seawater Sulfate Reducing Membrane (SWSR) is an NF membrane developed for seawater sulfate removal. It is built on GE’s robust DK membrane platform, which has been used for over 30 years in some of the most challenging applications. The SWSR Nanofiltration membrane features a 300 Dalton Molecular Weight cut-off and is an absolute barrier for any suspended matter including particles, colloidal silica, and bacterial matters. Additional benefits include:



- Prevents strontium and barium sulfate scale in injection wells
- Better well souring mitigation by reducing the incoming sulfate
- Optimized for use in seawater while providing superior hydrodynamics, which result in longer membrane life
- Unique and long-proven GE 3-layer membrane structure that minimizes surface roughness and adherence
- Available in a 440 sq. ft. version to maximize membrane area for new systems while minimizing footprint
- Superior hardness and sulfate removal properties
- Chemical compatibility with cleaners currently used in the industry
- Innovative spacer design combined with 3-layer membrane allows improved fouling resistance
- Can be combined with RO membrane arrays in order to provide low TDS water with specific divalent ion concentrations

## Importance of Pretreatment: Ultrafiltration

Sulfate removal units require pretreatment of seawater for removal of suspended solids and contaminants prior to entering the NF membrane system. Typical pretreatment technologies have included cartridge filters, multimedia filters or a combination of both. More recently, ultrafiltration has been gaining momentum with Oil & Gas Operators given the inherent benefits of a tighter pore structure coupled with an automated cleaning / back pulsing function.

Ultrafiltration is a type of membrane filtration process where the nominal pore size of the membrane is  $<0.1\mu\text{m}$ . Anything larger than the membrane pore size is prevented from passing through the membrane. Ultrafiltration removes large particles, bacteria, viruses and suspended solids but allows passage of dissolved organics and salts. Since salts are not rejected by the membrane there is a negligible osmotic pressure difference therefore UF is a low pressure process (operating at transmembrane pressures of less than  $\sim 2$  barg). UF membranes require backwashing and maintenance cleaning to restore the trans-membrane pressure (TMP) as well as Clean-in-Place (CIP) cycles to completely restore the TMP.

Ultrafiltration is a well-established technology in a number of different applications in both industrial and municipal segments. The technology is appealing to Upstream Oil & Gas operators given the link between improved pre-treatment and NF membrane performance and life. The importance of good quality pretreatment that maintains SDI levels below 3 have been demonstrated to have a positive impact on both RO and NF systems. UF, which typically has an effluent quality with an SDI of less than 2, is ideally suited to pretreat the water in front of the NF membranes. In addition to the aforementioned benefits, UF also allows decreasing the size and weight of the entire system, requires very little maintenance and is able to accommodate a good amount of variability in incoming water quality.

GE's ultrafiltration (UF) hollow-fiber membranes are designed with a robust life expectancy, giving confidence in the water treatment system's operation. GE's UF membranes are utilized in many different markets and applications, including Reverse Osmosis (RO) and Nanofiltration (NF) pretreatment. GE offers both pressurized and submerged technologies,

both of which can provide unique advantages depending on the unique characteristics of each Sulfate Removal project.

## GE's Ultrafiltration Membrane

GE's pressurized UF membrane is ideal for pretreatment applications for brackish and seawater desalination. Our membrane utilizes low-fouling PVDF membrane chemistry, resulting in less frequent and less aggressive cleaning. The pressurized membrane is optimal for packaged plants and pre-engineered designs with quick delivery and installation, and is also available as a custom solution engineered to specifications.

GE's immersed UF membrane system is ideal for retrofits and pre-treatment to reverse osmosis and nanofiltration systems. It allows producing a water quality that meets stringent standards while using less chemicals and reducing physical footprint. The cassettes and module materials are designed to operate in high salinity environments and minimize the number of process components and connections.

## Conclusions and Final Thoughts

Sulfate removal units (SRUs) are an established process to prevent scale formation in the reservoir. A typical SRU will consist of trains of NF membranes that will decrease the levels of incoming sulfate from 2700ppm to below 40ppm. Decreasing sulfate also eliminates the substrate for sulfate reducing bacteria thereby decreasing reservoir souring and equipment complications related to corrosion. Nanofiltration can also be used to economically remove hardness ions from seawater, which may be desirable in certain reservoir formations or where dilution water is required for polymer flooding. The selectivity of NF membranes to separate hardness ions from seawater is found to be best at a pH below 7, preferably in the range 5-6 and is dependent on NF membrane morphology and its intrinsic properties. Continuous long-term operation of sulfate removal units is improved with consistently excellent pretreatment, preferably ultrafiltration.

Contact GE Water & Process Technologies to find out more about our innovative water management solutions for the upstream Oil & Gas industry.

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