SUEZ membrane technology proven for sulfate removal in seawater

background

Compromised formation permeability and reservoir souring are two potential issues faced by oil and gas companies and operators. Offshore, these issues are caused by the interaction of sulfate ions present in seawater with barium (Ba) and strontium (Sr) in subsea reservoirs. Sulfate removal is critical in these applications as it prevents loss of reservoir productivity; removal also limits the substrate needed for the sulfate-reducing bacteria to produce hydrogen sulphide gas which causes reservoir souring.

SUEZ recently teamed with Petrobras to pilot a seawater sulfate removal (SWSR) nanofiltration (NF) membrane that provides superior hydrodynamics and excellent sulfate and hardness removal properties in seawater (see Figure 1). SUEZ's SWSR-440 NF membrane features a unique, proven three-layer structure that minimizes surface roughness and fouling adherence when rejecting divalent ions.

Figure 1: SUEZ's SWSR NF membrane pilot operation

system specifics

The two-stage NF pilot system consisted of two housings of three elements each feeding a single housing of three elements. The elements included SUEZ's full-size 8-inch SWSR 440ft^2 NF membrane. Figure 2 provides the process flow diagram for the SWSR test system.

Seawater was continuously pumped to the feed tank to ensure that the pilot unit was always supplied with new seawater. Continuous water supply prevented temperature escalations and diminished the potential for bacterial contamination.

A pump connected to the feed tank maintained the 2.5 to 4 bar of feed pressure to the high pressure NF pump that moved the water through the NF pilot system. To ensure that the right amount of sulfate was maintained at the feed, a portion of permeate was recycled to the feed tank and mixed. The amount of recycle was determined by a mass balance around the permeate, reject and feed streams in order to simulate the same conditions as seen in the lag elements of a true SRU system.

The chemical program was adjusted to take into account the amount of chemicals recycled in order to determine the appropriate dosage rates. The pilot unit included three different chemicals: Hypersperse* MDC150 dosed continuously to prevent membrane scaling, BioMate* MBC2881 dosed intermittently to prevent biofouling, and BetzDearborn* DCL30 dosed as needed to neutralize chlorine in the feedwater.

All of the chemicals used in the pilot study are approved for full-size sulfate removal units on offshore platforms and are commonly used in many sulfate reducing units (SRUs) around the world.

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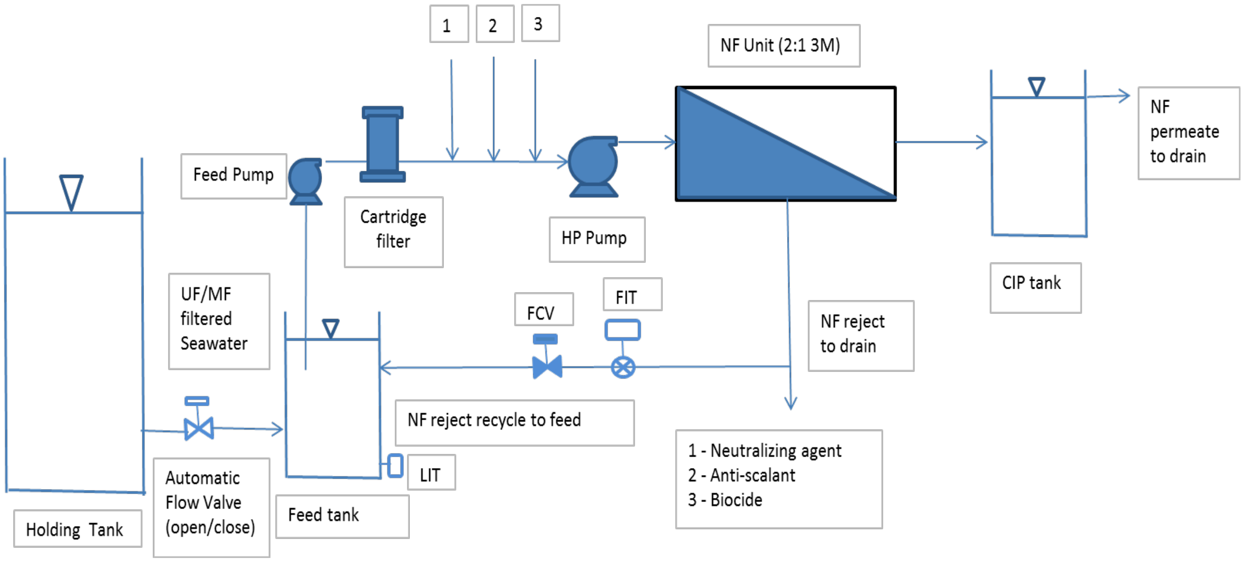

Figure 2: Process flow diagrarm of SUEZ's SWSR test system

The system also included a clean-in-place (CIP) cycle that was initiated when one of the following occurred: 1) normalized feed pressure increased 15 percent compared to initial performance, 2) normalized pressure drop increased 15 percent in either stage, 3) sulfate levels in the permeate exceeded a threshold value corresponding to less than 99.5% rejection.

test protocol

The pilot ran at the specified flux of 11.4 gal/d/ft^2 (gfd), 19.38 liter/m^2/h (lmh), and feed sulfate values of 5900 mg/L. This simulated the flux and recovery of the lag elements (stage 2) of a full-scale 2:1 array SRU operating at 15 gfd, 25.5 lmh, a sulfate feed of 2700 mg/L, with an overall recover of 75 percent. Operating conditions were adjusted, as necessary, to ensure a direct correlation between the performance of the 2:1 pilot and the expected performance in the actual SRU.

InSight*, SUEZ's cloud-based remote monitoring solution, automatically collected data at 1-minute intervals for system pressure, flow, conductivity, and temperature.

Feed and permeate/product analytical sampling was performed on a regular basis under stable conditions and additional analytical testing monitored performance, chemical dosing, and discharge.

results

SUEZ's SWSR-440 NF membrane demonstrated greater than 99.8 percent sulfate rejection during the initial stage of the pilot. Despite the high feed sulfate concentration (5500 ppm to 6100 ppm), permeate sulfate levels were at or below 10 ppm during the first four months of operation.

The average silt density index (SDI) of the system's feedwater remained around 2.5 during the first six weeks of operation, but increased to more than four during the remainder of the pilot. Higher SDI affected NF membrane performance in terms of feed pressure and differential pressure, but did not affect the permeate water quality.

While some industry findings have reported significantly lower sulfate rejection in feedwater with a pH higher than 7, SUEZ's SWSR-440 NF elements showed excellent sulfate rejection with a feedwater pH consistently above 8.

After four months of operation, the pressure drop started increasing and a CIP cycle was performed. Immediately after CIP, permeate sulfate concentration increased to 15 ppm (99.7 percent rejection) before decreasing back down to 10 ppm over the three weeks that followed. This occurrence was expected and is attributed to the opening of membrane pores under alkaline clean and closing of pores under acidic clean. By using a stronger acid one can further constrict the pores post CIP to potentially obtain a sulfate rejection closer to 10 ppm. Figure 3 shows sulfate rejection levels and their gradual return to 99.8 percent rejection.

Besides excellent sulfate rejection, the SWSR NF membrane showed superior hardness rejection properties. Total rejection at the beginning of the pilot was 94 percent (see Figure 4) with calcium (Ca) and magnesium (Mg) rejection at 87 percent and 95 percent, respectively (see Figures 5 and 6). Mg rejection decreased from 95 percent to 92 percent and Ca rejection decreased from 86 percent to 82 percent during the first four months of operation.

Total hardness rejection decreased further to 90 percent after CIP; Ca rejection decreased from 82 percent to 74 percent and Mg rejection decreased from 92 percent to 90 percent (see Figures 5 and 6).

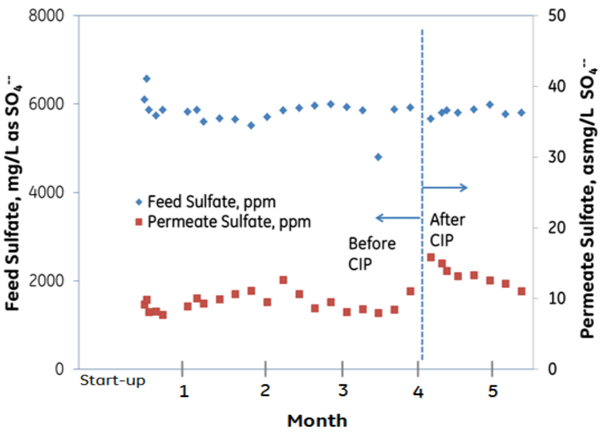

Figure 3: Feed and permeate sulfate concentration

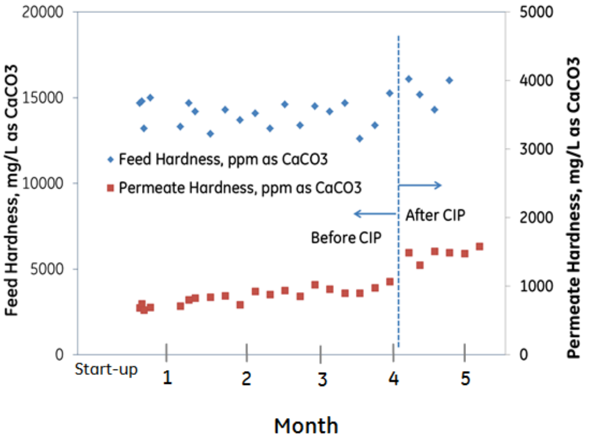

Figure 4: Feed and permeate hardness concentration

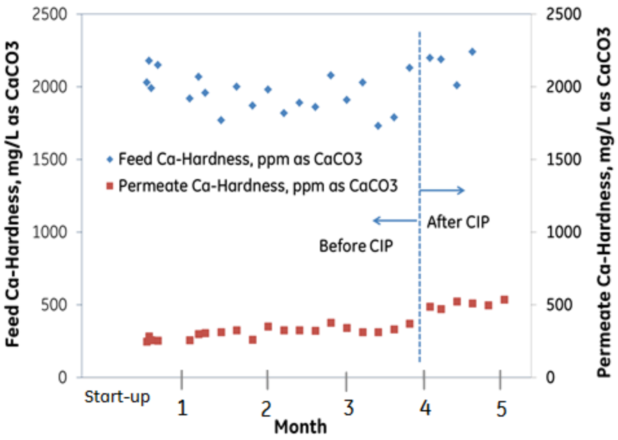

Figure 5: Feed and permeate Ca hardness concentration

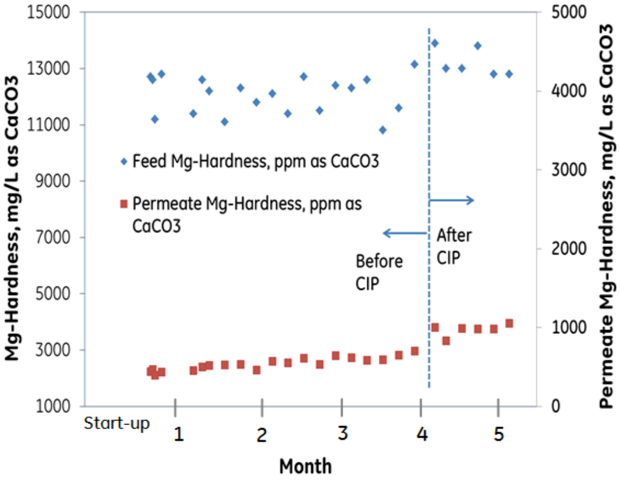

Figure 6: Feed and permeate Mg hardness concentration

Feed pressure was found to be a function of three parameters:

- Feedwater quality (SDI) – feed pressure increased as the SDI increased from less than 2.5 to more than 4.
- Feed temperature – feed pressure increased when the temperature decreased
- Feed conductivity – feed pressure increased when conductivity increased.

All three, impacted feed pressure, causing it to gradually increase over the pre-CIP 4 month period. Once the CIP was performed, feed pressure was restored to its initial value of 15 bar (see figure 7).

Differential pressure is another good indicator of membrane performance in terms of fouling potential. As the feedwater SDI increased (from 2.5 to about 4), the differential pressure across the membranes increased as well to 1.3 bar. This observed increase in differential pressure represents very stable membrane performance considering the high salinity, high SDI water with high scaling potential (high Ca, Mg, and SO_4 concentration).

Membrane Clean in Place

Membrane cleaning was initiated after 4 months of operation given the gradual increase in pressure drop from 1 to 1.3 bar, despite permeate sulfate levels consistently at or below 10ppm (99.8% rejection). We attribute this excellent sulfate rejection to membrane chemistry and SUEZ's proprietary 3-layer design, which together have historically proven to minimize adherence and maximize sulfate and hardness rejection. In addition to the increase in pressure drop, the decision to initiate a CIP was also driven by an increase in SDI and feed pressure.

To evaluate the impact CIP had on operational performance, permeability tests were conducted at five different flow rates. The CIP recovered 10 percent or more feed pressures at all tested rates. Upon the restart of the pilot, feed pressure was found to be 15 bar, which is in line with what was observed during the initial stages of the pilot, indicating full recovery.

CIP also reduced pressure drop across the membrane by about 10 percent (see Figure 8), back to the 1.2 bar baseline that was observed at month 2. The increase in pressure drop from month 1 to month 2 in figure 8 is consistent with the rapid increase in SDI of the seawater feed (2.5 to over 4). This increase was due to a change in pre-treatment performance that stabilized after the second month for the remainder of the pilot test at an SDI of 4. It is also worth mentioning that both first and second stage pressure drops decreased with a marginally higher recovery observed in the first stage.

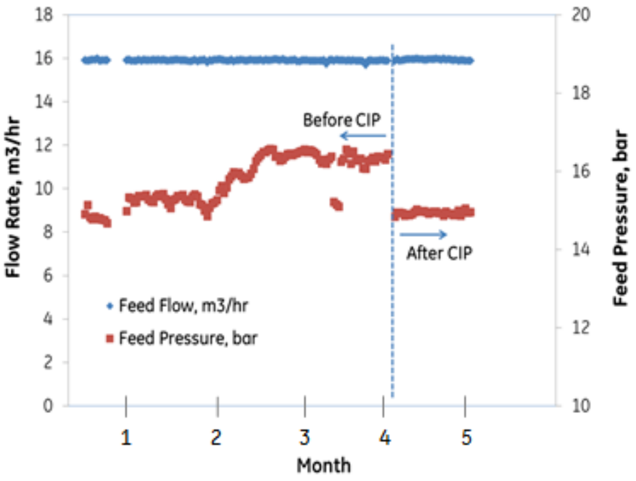

Figure 7: Feed pressure before and after CIP

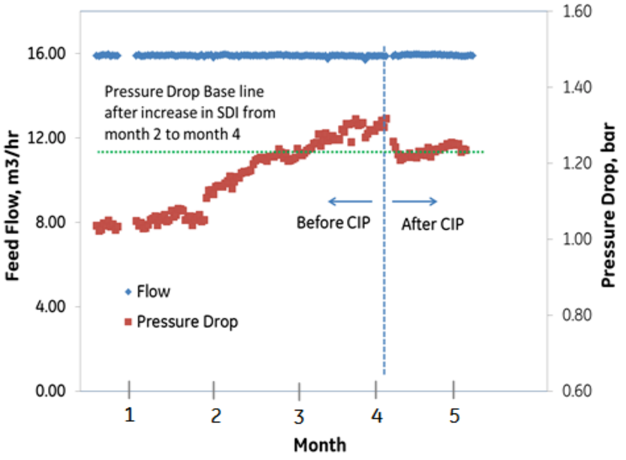

Figure 8: Pressure drop before and after CIP

conclusion

Overall, the pilot confirmed the excellent sulfate rejection properties of SUEZ's SWSR NF membrane, even with challenging feedwater quality and high sulfate concentrations. The unique three-layer construction resists fouling and demonstrates excellent recoverability when subjected to a standard CIP procedure identical to what is seen on full scale offshore sulfate removal units.

Petrobras was impressed with the membrane's ability to perform even under the most challenging of conditions and approved SUEZ's SWSR solution for seawater sulfate removal for their offshore installations.