

Veolia membrane technology proven for sulfate removal in seawater

CASE STUDY | Upstream Oil & Gas/E & P

| 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 sulfide gas which causes reservoir souring.

Veolia 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). Veolia's SWSR-440 NF membrane features a unique, proven three-layer structure that minimizes surface roughness and fouling adherence when rejecting divalent ions.

| 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 Veolia's full-size 8-inch SWSR 440ft² 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.



Figure 1: Veolia's SWSR NF Membrane Pilot Operation

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.

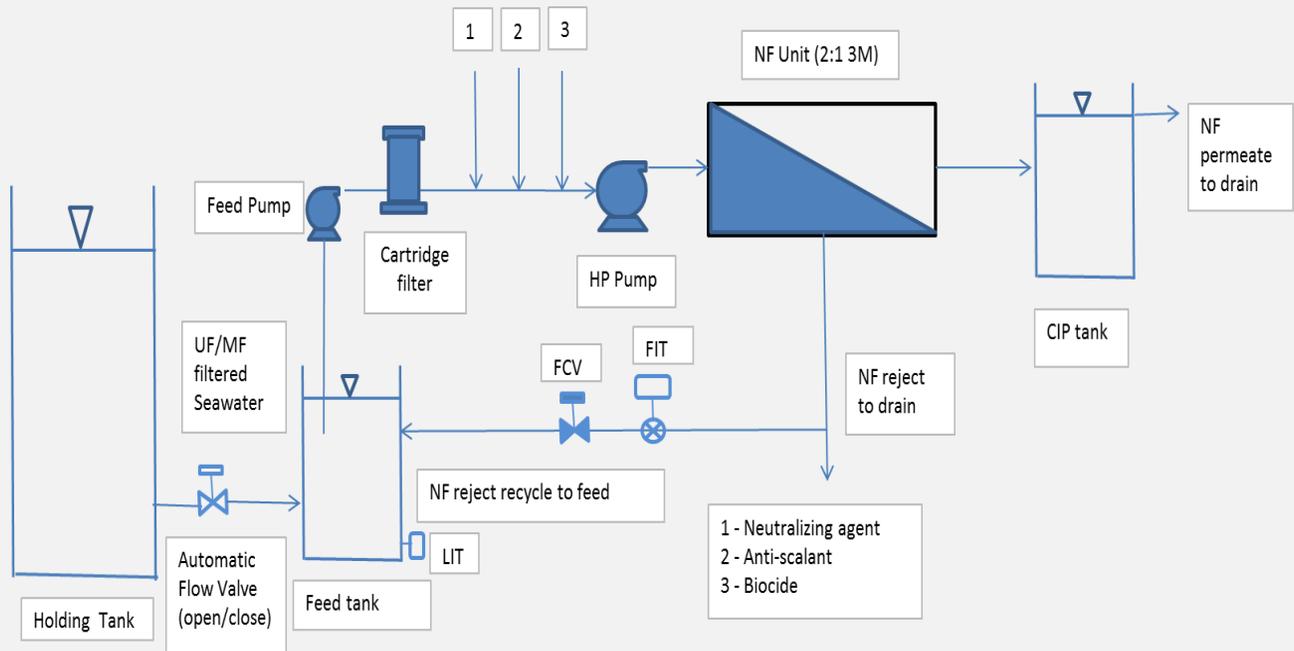


Figure 2: Process flow diagram of Veolia's SWSR test system

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/ft² (gfd), 19.38 liter/m²/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*, Veolia'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

Veolia'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, Veolia'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% 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% 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).

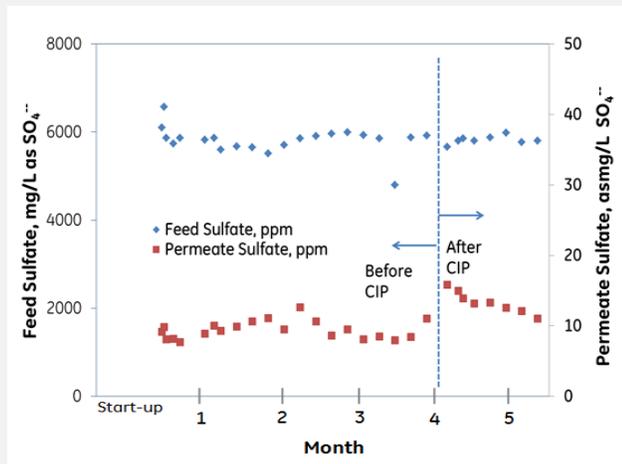


Figure 3: Feed and Permeate Sulfate Concentration

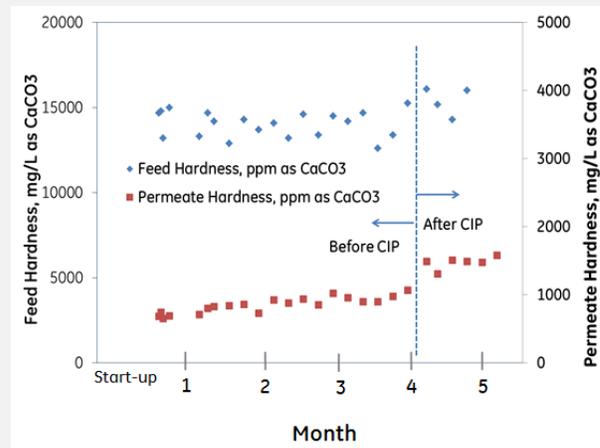


Figure 4: Feed and Permeate Hardness Concentration

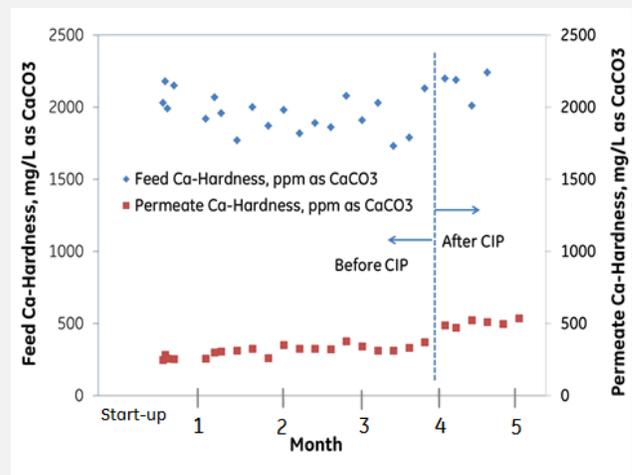


Figure 5: Feed and Permeate Ca Hardness Concentration

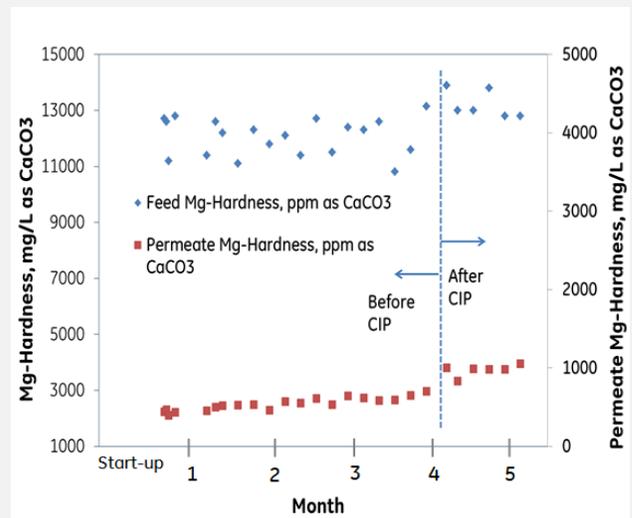


Figure 6: Feed and Permeate Mg Hardness Concentration

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 SO₄ concentration).

Membrane Clean in Place

Membrane cleaning was initiated after four 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 Veolia'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.

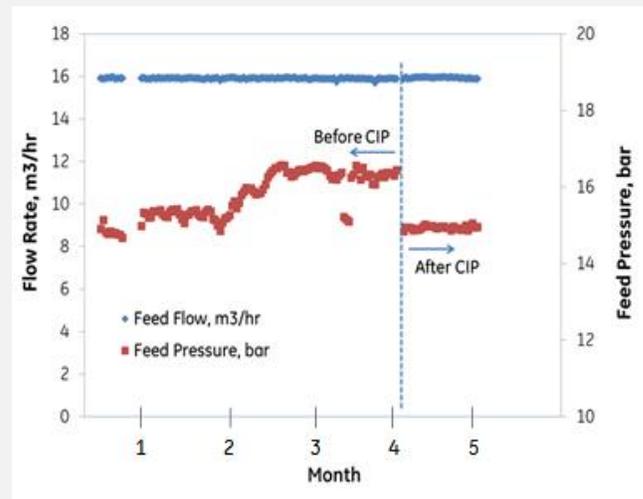


Figure 7: Feed pressure before and after CIP

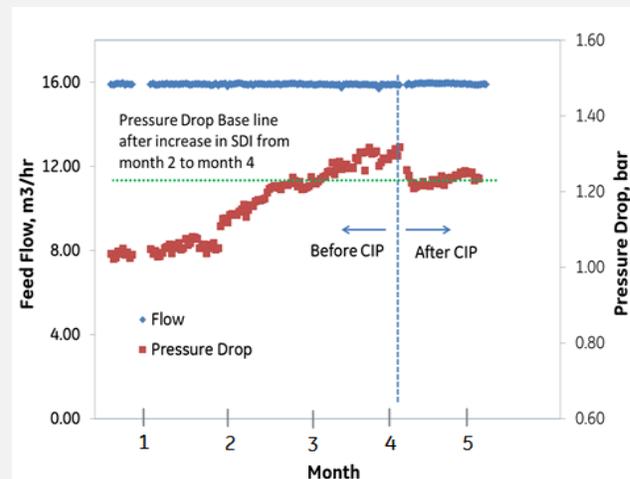


Figure 8: Pressure drop before and after CIP

Conclusion

Overall, the pilot confirmed the excellent sulfate rejection properties of Veolia'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 Veolia's SWSR solution for seawater sulfate removal for their offshore installations.

Removal of sulfate in the chlor-alkali industry with spiral-wound membrane elements

TECHNICAL BULLETIN

Introduction

In the chlor alkali industry, sodium hydroxide (NaOH; caustic), chlorine gas (Cl₂), and hydrogen are produced as a result of electrolysis of NaCl. The primary product is chlorine and caustic as they are building block compounds for thousands of useful products.

Predicted global values of chlorine and NaOH market will continue to grow at a compound annual growth rate (CAGR) of 6.5% and 4.6% over the 2017-2022 forecast period, reaching US\$42 and 42.8 billion in 2022, respectively.

Application/Background

There are three distinct types of electric processes used in the production of chlorine: (i) diaphragm cell process, (ii) mercury cell process, and (iii) membrane cell process. There are significant technical differences between the three. One of the important differences between these technologies is in brine purification steps. Mercury and diaphragm, compared to membrane cell process technologies, do not require brine with very high purity. Precipitation and filtration are adequate for diaphragm and mercury cell processes, but for membrane cell process, secondary treatment of brine with ion exchange resin might need to be carried out. Depending on the source of the NaCl brine, it may contain mercury and up to 20 g/l Na₂SO₄.

In 2016 European chlorine producers released a total of 1.4 metric tons of mercury into the atmosphere. Therefore, European Union regulation required companies to stop making Chlorine via a process that involves mercury by the end of 2017.

Value Proposition

Nanofiltration (NF) membranes can be chosen with high affinity to Na₂SO₄ rejection, allowing to recirculate the NaCl brine more effectively. Implementation of nanofiltration results in the following:

1. **Environmentally friendly:** Replaces BaCl₂, BaCO₃, CaSO₄.
2. **Lower CAPEX:** Certain methods (chemical precipitation, ion exchange, crystallization, and purging) to remove impurities such as sulfate are capital-intense and difficult to implement effectively in terms of techniques or environmental constraints.
3. **Lower OPEX:** Lowers plant salt/chemical consumption by >20%. Reduces CaCl₂ addition, improves gypsum economics, so less chemical to precipitate sulfate and less sludge to be disposed.
4. **Lower OPEX:** Removing Na₂SO₄ deposits near cathode surface results reduced cell (anode) current efficiency and purity of Chlorine gas as sulfate releases oxygen at the anode.
5. **Feasibility:** Works in membrane, diaphragm, or mercury plants.
6. **Efficiency:** Reduces NaCl loss and effluent flow compared to purging and increases ion-exchange membrane.

Case Study

NF feed:

- ~170-230 g/l NaCl
- ~6-20 g/l Na₂SO₄; ~4-11 g/l NaClO₃
- pH: 8-10; Temperature: 40-50 °C
- Density: ~1100 kg/m³

NF System:

- Elements type:
 - DK-400 or DK-440 if Temperature is below 50 °C
 - Durathem Excel NF HR if Temperature is below 70 °C
- Pretreatment: 1-micron pre-filters and activated carbon

Typical array and recovery: 4:3:2:1, 4/3:2:1, 2:1:1, 1:1:1, 1:1 depending on Na₂SO₄ load; 5 element per vessel and over 90% recovery.

Veolia Water Technologies

Please contact us via:

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WATER TECHNOLOGIES

DK Series

FACT SHEET

Industrial High Rejection Nanofiltration Elements

The D-Series family of proprietary thin-film nanofiltration membrane elements is characterized by an approximate molecular weight cut-off of 150-300 Dalton for uncharged organic molecules. Divalent and multivalent anions are preferentially rejected by the membrane while monovalent ion rejection is dependent upon feed concentration and composition. Since monovalent ions pass through the membrane, they do not contribute to the osmotic pressure, thus enabling D-Series nanofiltration membrane systems to operate at feed pressures below those of RO systems.

Among other applications DK High Rejection NF Elements are used for dye removal/concentration, sodium chloride diafiltration and metals recovery.

Table 1: Element Specification

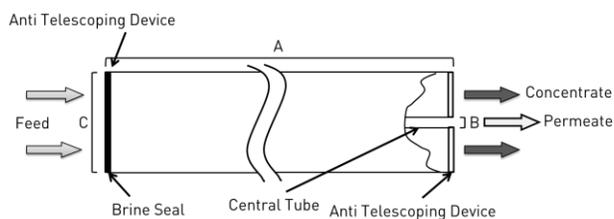
Membrane	D-Series, Thin-film membrane (TFM*)	
Model	Average Permeate Flow gpd (m ³ /day) (1,2)	Minimum MgSO ₄ Rejection (1,2)
DK2540C30	560 (2.1)	98%
DK2540C50	350 (2.3)	98%
DK2540F30	540 (2.0)	98%
DK2540F50	340 (1.3)	98%
DK4040C30	1,900 (7.2)	98%
DK4040C50	1,400 (5.3)	98%
DK4040F30	1,900 (7.2)	98%
DK4040F50	1,400 (5.3)	98%
DK8040C30	8,100 (30.7)	98%

DK8040C50	6,500 (24.6)	98%
DK8040F30	8,100 (30.7)	98%
DK8040F50	6,500 (24.6)	98%

(1) Average salt rejection after 24 hours operation. Individual flow rate may vary ±25%

(2) Testing conditions: 2,000ppm MgSO₄ solution at 110psi (760 kPa) operating pressure, 77 °F (25°C), 15 % recovery.

Model	Spacer mil (mm)	Active Area ft ² (m ²)	Outer Wrap	Part Number
DK2540C30	30 (0.76)	24 (2.2)	Cage	1206918
DK2540C50	50 (1.27)	18 (1.6)	Cage	1206919
DK2540F30	30 (0.76)	28 (2.6)	Fiberglass	1206925
DK2540F50	50 (1.27)	22 (2.0)	Fiberglass	1206926
DK4040C30	30 (0.76)	89 (8.2)	Cage	1206947
DK4040C50	50 (1.27)	67 (6.2)	Cage	1206946
DK4040F30	30 (0.76)	85 (7.9)	Fiberglass	3050075
DK4040F50	50 (1.27)	65 (6.1)	Fiberglass	3050073
DK8040C30	30 (0.76)	374 (34.7)	Cage	1206978
DK8040C50	50 (1.27)	300 (27.9)	Cage	1206979
DK8040F30	30 (0.76)	364 (33.8)	Fiberglass	1206993
DK8040F50	50 (1.27)	284 (26.4)	Fiberglass	1206994



Note: **4040C** elements do not feature brine seal.

Figure 1: Element dimensions diagram – female

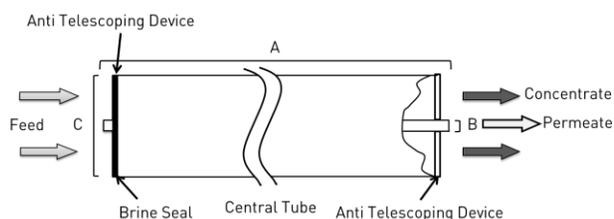


Figure 2: Element dimensions diagram – male

Table 3: Operating and CIP Parameters

Typical Operating Flux	5 - 20 GFD (8 – 34 LMH)
Maximum Operating Pressure	600psi (4,137kPa) if T<95°F (35°C) 435psi (3,000kPa) if T>95°F (35°C)
Maximum Temperature	Continuous operation: 122°F (50°C) Clean-In-Place (CIP): 122°F (50°C)
pH Range	Continuous operation: 3 – 9 Clean-In-Place (CIP): 2 – 11 (1)
Maximum Pressure Drop	Over an element: 15psi (103 kPa) Per housing: 60psi (414kPa)
Chlorine Tolerance	500 ppm hours, dechlorination recommended
Feedwater	NTU < 1 SDI15 < 5

(1) Refer to Cleaning Guidelines Technical Bulletin TB1194.

Table 2: Dimensions and Weight

Model	Fig.	Dimensions, inches (cm)			Boxed Weight lbs (kg)
		A	B	C	
DK2540C**	2	40.0 (101.6)	0.75 (1.90)	2.4 (6.1)	4 (1.8)
DK2540F**	2	40.0 (101.6)	0.75 (1.90)	2.4 (6.1)	4 (1.8)
DK4040C**	1	40.0 (101.6) (1)	0.625 (1.59)	3.9 (9.9)	11 (5)
DK4040F**	2	40.0 (101.6)	0.75 (1.90)	3.9 (9.9)	11 (5)
DK8040C**	1	40.0 (101.6)	1.125 (2.86)	7.9 (20.1)	35 (16)
DK8040F**	1	40.0 (101.6)	1.125 (2.86)	7.9 (20.1)	35 (16)

(1) Includes interconnector, refer to Technical Bulletin TB1206.