

Evaluation of DOW™ ultrafiltration operation at low temperatures

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ABSTRACT

Ultrafiltration is a pressure-driven technology which provides consistent and reliable filtrate water with low Silt Density Index (SDI), independently of the feed water source. For sea water applications, the feed may vary a lot depending on the location and the season. Ultrafiltration should be able to process very cold water in the Nordic countries which can be below 5°C during the winter to very warm water in the Middle East reaching up to 40°C during the summer. However, it is well-known that temperature has a high impact on pressure-driven UF technology due to water viscosity changes requiring higher pressure to overcome the resistance across the membrane. Apart from viscosity, other challenges that can be thought to affect the ultrafiltration operation at low temperature are the cleaning efficiency with chemicals such as sodium hypochlorite and the possible effect of temperature on porosity of the fiber material. An experiment was performed at the DW&PS Global Water Technology Center in Tarragona (Spain) in order to evaluate if DOW™ Ultrafiltration SFP-2880 modules can sustainably operate with seawater at cold temperatures. The commercial UF modules consisted of modified Hydrophilic-PVDF fibers of 0.03 mm of nominal pore diameter housed in an uPVC casing. The feed water for the experiment was Mediterranean Sea Water from the Tarragona harbor which temperature was adjusted using a cooling system at different set points of 5°C, 12°C and 25°C. From this study was concluded that Dow hydrophilic-PVDF fiber had similar behavior at temperatures between 5°C and 12°C than at 25°C showing stable operation over two months with constant trans-membrane pressure (TMP) and permeability. Although, a higher feed pressure is required when working at lower temperatures due to higher water viscosity, when normalized to 25°C, the TMP and the permeability trends are similar as during operation at higher temperatures.

Keywords: Low temperature; Membranes; Pre-treatment; Seawater; Ultrafiltration

1. Introduction

Ultrafiltration is a pressure-driven technology which provides consistent and reliable filtrate water with low Silt Density Index (SDI), independently of the feed water source. For seawater applications, the feed may vary a lot depending on the location and the season. Ultrafiltration should be able to process very cold waters such as in the Nordic countries which can be below 5°C during the

winter to very warm waters like in Middle East reaching up to 40°C in summer time. However, it is well-known that temperature has a high impact on pressure-driven UF technology due to water viscosity increases requiring higher pressure to overcome the resistance across the membrane. When operating at low temperatures, water viscosity increases reducing considerably the water permeability as well as significantly increasing the trans-membrane pressure (TMP).

These challenges are highly present in some locations as in the North Sea, where the seawater temperature is very

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low, especially in the winter. The North Sea, is one of the most populated seas in terms of offshore platforms, which use seawater as feed for water injection processes through the wells. Water injection processes may include a pretreatment such as Ultrafiltration, followed by sulfate removal membranes in order to remove the sulfate content prior to injecting the water into the oil well. Water treatment processes will be affected depending on sea water temperature. North Sea surface temperature typically ranges, according to recorded measurements, from 17°C to 8.5°C. On the other hand, the temperatures at the sea bottom are rather lower, ranging from 7.8°C to 5.4°C [1].

Apart from viscosity, other challenges that may affect the ultrafiltration operation at low temperatures are the cleaning efficiency with sodium hypochlorite. It is typically well known that cleanings using chemicals are more efficient at higher temperatures. Temperature may affect membrane cleaning by changing the chemical reaction, the kinetics and the solubility of the chemicals. A study at different temperatures monitoring the flux recovery after cleanings at different temperatures showed that the cleaning at 12°C was not as effective as when it was carried out at 20°C and 29°C. Moreover, an increase of cleaning duration shows an improvement of flux recovery following a logarithmic curve tendency [2].

1.1. Background

Temperature has a high impact on the membrane filtration process mainly due to water viscosity changes. As water temperature decreases, the viscosity of water increases. At higher viscosities, membrane requires higher pressure to overcome the resistance across the membrane. Because of this, the effect of the viscosity should be taken into consideration when any facility is designed in order to ensure the adequate production capacity over the whole year. In addition, if temperature is not considered when evaluating the operational data, an increase in pressure can be misinterpreted as fouling problem on membrane surface.

Fig. 1 represents how the water viscosity is changing along different temperatures. As observed in Fig. 1, when the temperature decreases the viscosity increases. The relation between both parameters is not linear at all temperature ranges, especially at low and high temperatures.

Temperature effect can be considered when assessing the evolution of the parameters typically used to monitor

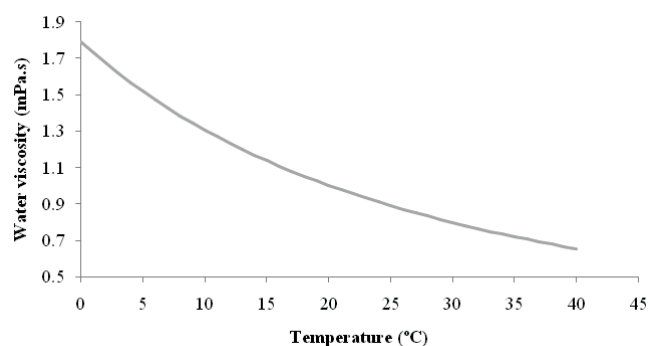


Fig. 1. Water viscosity at different temperatures. [Source: own elaboration using IAPWS coefficients].

the performance of an UF system, i.e., TMP and permeability. The TMP is calculated as the difference between feed pressure and filtrate pressure, while the water permeability is defined as the ratio between the operational flux (flow/filtration area) and the TMP. In order to normalize both TMP and permeability to consider the temperature effect, it is needed to calculate the Temperature Correction Factor (TCF). The TCF formula takes into account the liquid water viscosity at different temperatures. The formula used is given by the International Association for the Properties of Water and Steam (IAPWS) for liquid water between 253.15 and 383.15 K [3] (American Water Works Association) where T_k means temperature in Kelvin (see Eq. (1)). The TCF factor is multiplied by the raw TMP in order to get the normalized TMP (see equations below):

$$TCF = \frac{890}{\left(280.68 \left(\frac{T_k}{300}\right)^{-1.9}\right) + \left(511.45 \cdot \left(\frac{T_k}{300}\right)^{-7.7}\right) + \left(61.131 \cdot \left(\frac{T_k}{300}\right)^{-19.6}\right) + \left(0.45903 \cdot \left(\frac{T_k}{300}\right)^{-4.0}\right)} \quad (1)$$

$$\text{Normalized TMP (bar)} = \text{Actual TMP} \cdot \text{TCF} \quad (2)$$

$$\text{Normalized permeability} \left(\frac{L}{m^2 h bar} \right) = \frac{\text{Actual permeability}}{\text{Normalized TMP}} \quad (3)$$

1.2. Objectives

The objectives of the present experiment are:

- Understand the performance of Ultrafiltration at different temperatures, from very cold sea water below 5°C to warm water at 30°C.
- Evaluate which are the challenges associated with very low temperatures. Three main parameters are considered: water viscosity effect, cleaning efficiency and material properties.

2. Materials and methods

This research was conducted at the Dow Water and Process Solution Global Water Technology Center (GWTC) in Tarragona, Spain. The feed water was seawater from the Mediterranean Sea.

A pilot unit consisting of Ultrafiltration and followed by a Reverse Osmosis system was used for this project. Two DOW Ultrafiltration SFP-2880 modules were installed in the pilot unit for this purpose. The RO unit consisted of two pressure vessels of four inches diameter with capacity for three RO elements working in series.

Before feeding to the UF, the sea water was cooled down using a cooling system with glycol as a refrigerant. The sea water was refrigerated in once-through mode, from sea temperature to a minimum of 5°C. Fig. 2 below shows the pilot plant scheme. This paper will only cover the operation of the UF at low temperature. The operation of RO unit at low temperature was not evaluated.

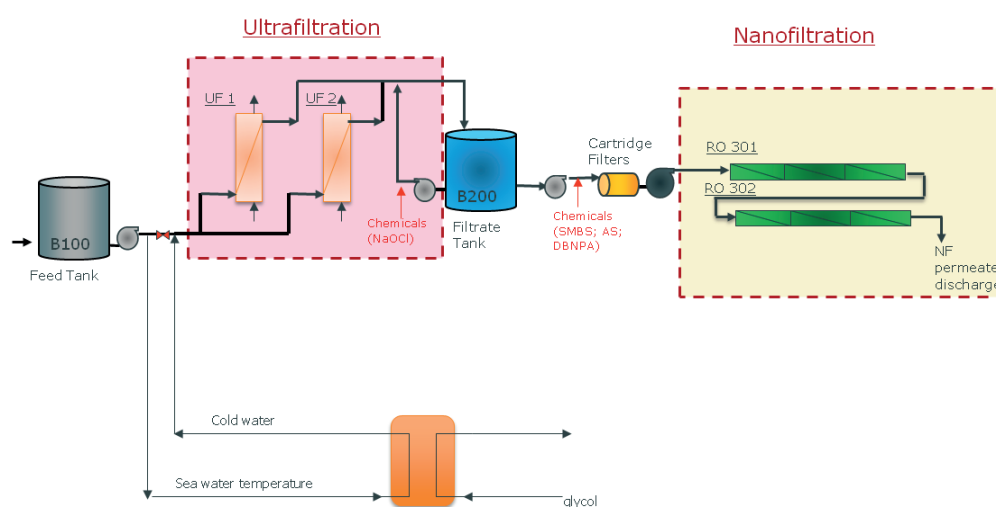


Fig. 2. Pilot plant scheme.

The UF modules were commercial DOW™ SFP-2880 with 77 m² surface area. The hollow fiber material consisted of modified Hydrophilic-PVDF fibers of 0.03 mm of nominal pore diameter housed in an uPVC casing. The PVDF is a very flexible and robust material with excellent break resistance and superior tolerance to chlorine compared to other UF materials such as PS/PES or PP. The UF flow pattern was out-in; thus, feed water entered from the outer wall through the UF fiber and filtrate was collected in the inside lumen. The hollow fiber membrane had an outside diameter of 1.3 mm and inside diameter of 0.7 mm. The project was divided in two different tests:

- *Temperature test*: short test covering the temperature spectrum between 5°C and 30°C in order to evaluate the temperature effect on the UF. The test was done with sea water working in once-through mode and at constant operation flux of 70 L/m²h.
- *Long-term continuous operation*: it includes more than 4 months of data of DOW Ultrafiltration SFP-2880 operated at different temperatures. The test involved different cleanings: hourly backwashes (BW), daily chemically enhanced backwashes (CEBs) and three clean in place (CIP). Three different temperature ranges were evaluated during the experiment:
 - Temperature from 4.8°C to 8.5°C
 - Temperature from 7°C to 14°C
 - Temperature from 25°C to 29°C

During the experiment, weekly samples were analyzed in order to monitor the UF performance. The parameters analyzed were feed and filtrate turbidity.

3. Results and discussion

3.1. Temperature test

The temperature test was done with two UF modules. Fig. 3 below represents the TMP vs. the operation temperature. As it is observed, raw TMP increases

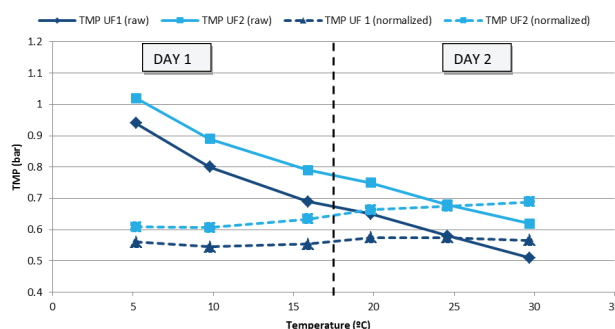


Fig. 3. TMP vs. temperature curve.

when temperature decreases. More in detail, at lower temperatures, the UF showed a TMP of 0.94 (module UF1) and 1.02 bar (module UF2). On the other hand, at 30°C, the raw TMP was 0.51 bar (module UF1) and 0.62 bar (module UF2). When applying the viscosity factor (Eqs. (1)–(3) above), the normalized TMP showed a practically flat tendency. It could be then concluded that the major effect that UF modules suffer when working at lower temperature is the water viscosity. There is no evidence that suggests any change of material properties affecting the UF performance at low temperatures apart from the expected effect of the water viscosity and the lower chemical cleaning efficiency.

3.2. Long-term continuous operation

Table 1 below summarizes the experimental conditions at which this part of the project was carried out. Filtrate production was the same during all the experiment (70 L/m²h). A standard cleaning protocol as recommended by Dow Water and Process Solutions was undertaken. It included hourly backwashes (BW's) and daily chemically enhanced backwashes (CEBs). Backwash fluxes were optimized during the experiment in order to achieve the optimal UF performance. Three cleaning in place (CIPs), including

Table 1
UF operation conditions

Parameter	Value
Temperature	Three different temperature ranges tested
Module	DOW™ SFP-2880
Filtration Flux	70 L/m ² h
Backwash (every 60 min)	<ul style="list-style-type: none"> • AS – 30 s • Drain – 30 s • BWT + AS – 100s^a • BWB + AS – 100s^a • FF + AS – 50s
Chemically Enhanced Backwash (every 24 h)	Chemical dosage – NaOCl, 350 mg/L aprox. Soaking – 510 s
Backwash after the CEB (every 24 h)	Same than hourly Backwash
Clean in place (three times)	0.2 % NaOCl; 1% oxalic acid Temperature: 35°C

^aDifferent backwash fluxes were tested during the experiment.

These are:

Day 0: 80 L/m²h
 Day 66: 100 L/m²h
 Day 85: 130 L/m²h
 Day 91: 100 L/m²h

caustic and acid steps, were also required. The CIP were done following DOW guidelines [4] at warm temperature of 35°C. Table 1 shows the operation conditions.

Fig. 4 shows the temperature along the experiment. Three different temperature ranges were tested: from 4.8°C to 8.5°C; from 7°C to 14°C and from 25°C to 29°C. The temperature variation in each of the ranges is produced by the seawater temperature differences between days and nights. Fig. 4 also shows the TMP along the days of operation. The graphic represents both, the raw data recorded from the system at the real operation temperature and the normalized TMP calculated at 25°C using Eq. (1) above. The operational temperature is as well also represented in the same graphic.

The initial TMP at low temperature of 6.1°C was 0.82 bar (raw TMP) and 0.56 bar (normalized TMP). The UF module used for this experiment was not brand new. Thus, the initial TMP may be slightly higher than a brand new element. Nevertheless, the module was cleaned by caustic and acid using standard CIP process before starting the experiment.

After 1 month of operation, it was observed a relatively fast increase of TMP water reaching 2.1 bar. This was caused by a change in the feed water quality, which suddenly reached high turbidity values around 50 NTU. Nevertheless, this high TMP value was recovered back after doing two standard CEB's.

In order to recover further the TMP to initial values of 0.56 bar (normalized TMP), a CIP was done. The CIP recovered the TMP back to the initial values. After the CIP,

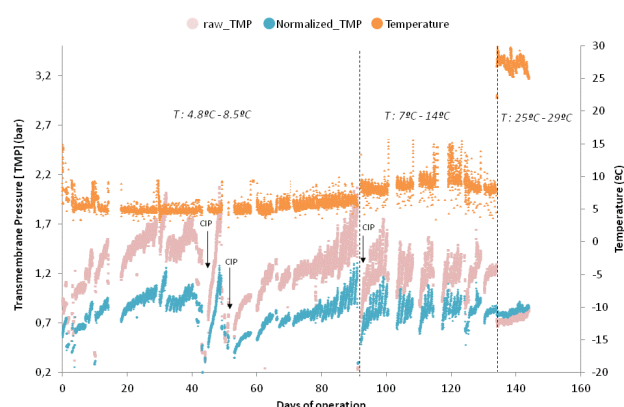


Fig. 4. Raw and normalized transmembrane pressure.

the unit was operated without CEB for 3 d, which again prompted the TMP to rise until reaching 2.1 bar.

- When working with sodium hypochlorite (for the CEBs) at low temperatures, it may precipitate blocking the dosage system. Thus, it is required more frequent system maintenance, being highly recommended to do preventive cleaning of the NaOCl lines.
- At low temperatures, frequent CEBs with sodium hypochlorite are still required to avoid reaching high TMP in short time period.
- When working at low temperatures, the cleaning trigger of 2.1 bar will be reached more frequently or earlier than when working at higher temperatures. Thus, the CIP frequency will be higher. Fig. 4 shows that when raw TMP at 5.3°C was 2.1 bar, the normalized TMP was still 1.3 bar.

On day 91, the average temperature was increased from 6.6°C to 10.5°C. At this second temperature range, it was still observed an important difference between raw and normalized TMP. However, the operation was stable for 40 d. On day 133, the cooling system was disconnected in order to allow the system to operate at normal seawater temperature (average 27°C). It was observed that at higher temperatures, the normalized TMP and the raw TMP are practically overlapping. According to this, it can be concluded that the UF was not be affected by the previous 4 months of cold temperature operation.

Fig. 5 shows the raw and normalized permeability for the entire experiment. The permeability had similar tendency than TMP. During the second temperature range, the permeability was really constant. Nevertheless, the raw permeability showed low values around 55 L/m²h bar.

During the operation, samples were taken once per week in order to evaluate the UF filtrate quality. Turbidity was analyzed in samples from the feed and filtrate streams.

Fig. 6 shows the feed and filtrate turbidity. During the experiment, the turbidity in the filtrate was lower than 0.1 NTU. Thus, as expected, it can be confirmed that the water quality is guaranteed independently of the operation temperature.

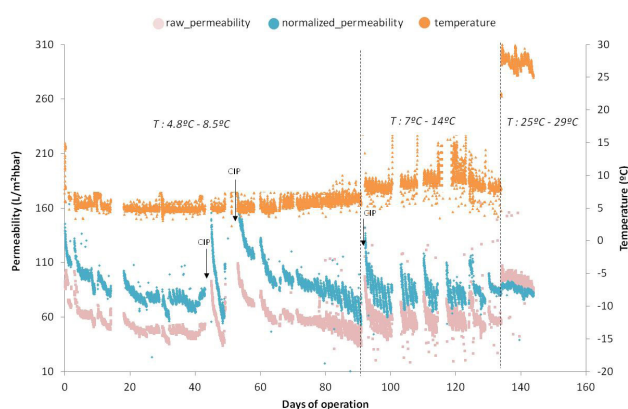


Fig. 5. Raw and normalized water permeability.

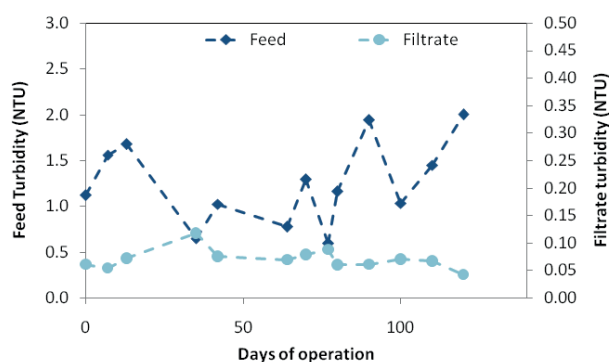


Fig. 6. Feed and filtrate turbidity.

Samples were taken during the sodium hypochlorite CEB in order to understand the chemical cleaning efficiency at low temperatures. Table 2 below shows chlorine measurements. As it can be observed, the samples analyzed showed different values of chlorine from 220 to 510 ppm being difficult to adjust the dosage at the recommended concentration of 350 ppm. Chlorine was also measured at the drain (once CEB soaking is finished) in order to understand the concentration of chlorine that was consumed during the cleaning. Results showed that the chlorine consumption during the cleaning was really low. Nevertheless, as observed before in Fig. 4, CEBs were needed to keep constant TMP values.

Fig. 8 shows part of the TMP recovered for each CEB at the different operation temperature. Values lower than 100% showed that CEB was not recovering the TMP to previous day TMP value. If recovery is higher than 100%, the CEB was reducing the TMP at values below than the previous day TMP (see Eq. (4)).

$$\text{TMP recovery (\%)} = \frac{\text{TMP after CEB}_{\text{Day } n-1}}{\text{TMP after CEB}_{\text{Day } n}} \quad (4)$$

Fig. 8 shows that the TMP recovery at lower temperatures shows high variation between one day to other day, being the minimum recovery of 92% and the maximum of 102%. Nevertheless, at higher temperatures between 25°C and 30°C, the TMP recovery is in all the cases higher than

Table 2

Chlorine analysis from different samples taken at different days of the project

Parameter	CEB dosage, ppm	CEB drain, ppm
Sample 1	290	206
Sample 2	220	166
Sample 3	450	390
Sample 4	570	520
Sample 5	510	500

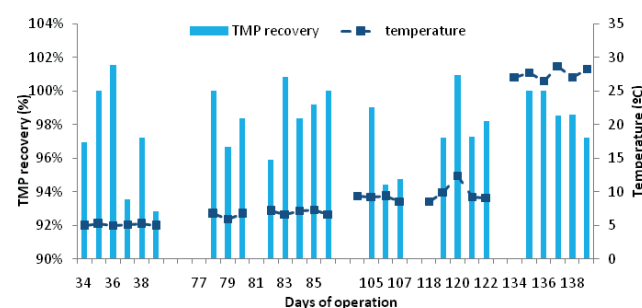


Fig. 8. TMP recovery.

97%. The slightly lower TMP recovery at cold water may be associated with the slower kinetics of the reaction at lower temperature. As observed in Table 2, at higher chlorine concentrations (i.e., sample 4 and 5) the chlorine consumption is similar than at lower chlorine concentrations (i.e., sample 1 and 2). Nevertheless, it is recommended an extensive further study on the chemical cleaning efficiency at lower temperatures.

4. Conclusions

Following conclusions can be extracted from this research project:

- DOW Ultrafiltration has been proven to be a robust technology to operate at a wide range of temperature.
- When working at low temperatures, water viscosity should be taken into consideration. TMP values measured will be high values and the permeability will be low. Despite this, sustainable UF operation is feasible.
- Chemical cleanings are still needed at low temperatures. In addition, operators need to take into consideration that the cleaning efficiency is closely related to the temperature at which it is carried out.
- When working at low temperatures, due to the water viscosity effect, the CIP cleanings will be required more frequently than at higher temperatures. As it was observed during the operation, the raw TMP will be higher at cold temperature than at warm temperature. Thus, the time needed by the TMP to reach the 2.1 bar which triggers the CIP is shorter.
- There is no evidence that may suggest any change of material permeability affecting the UF performance at

low temperature apart from viscosity and low chemical cleaning efficiency.

- Quality of the filtrate water was proven to be consistent and constant despite the wide range of temperatures evaluated within this research project.

Acknowledgments

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References

- [1] Met Office. (n.d.). *Metoffice*. Retrieved February 2015, Available online at: (<http://project.ncof.co.uk/B4G/indicator.php?indicator=ssst>)
- [2] C. Liu, S. Caothien, J. Hayes, T. Caothuy, Membrane Chemical Cleaning: From Art to Science, Pall Corporation, Port Washington, NY 11050, 2001.
- [3] American Water Works Association, Microfiltration and Ultrafiltration Membranes for Drinking Water. Manual of Water Supply Practices, First Edition. Copyright 2005 Denver, CO.
- [4] The Dow Chemical Company, Dow™ Ultrafiltration. General Design Guidelines, Available online at: (<http://www.dow.com/en-us/water-and-process-solutions>)