Report AquaSPICE

Case study at BASF Antwerp
Part I: Reuse of RO concentrate from the Demin plant

The Improved containers on site at BASF Antwerp - E527

Case study at BASF Antwerp: test period February – June 2023

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Contents

1. Abstract

During the first part of the BASF Antwerp trials for the AquaSPICE project, the IMPROVED containers were deployed for investigation of options to increase the water recovery of the newest demineralization plant of Evides Industriewater at BASF. The demin plant of Evides consists of double pass RO operated on softened Biesbosch surface water. A novel, closed-circuit reverse osmosis (CCRO) design by DuPont has been tested to reuse the first pass RO concentrate from the demineralization plant. The CCRO was implemented by modifying the conventional RO in the containers in accordance with the patent holder DuPont who allowed the modification exceptionally for UGent within the AquaSPICE trials. Hence, it should be noted that this CCRO is not a commercial configuration that DuPont typically licenses and there are potential differences from a typical commercial implementation of CCRO.

Additionally, the regeneration of the softener resins with the reverse osmosis (RO) concentrate of the demineralized water production plant was tested to use the RO brine instead of RO permeate in the resin regeneration process which would save water and marginally reduce the use of NaCl.

The tests showed that CCRO implementation on the RO brine could increase the overall recovery of the plant by 12 % (from current 85 to 97%). This will reduce the intake of Biesbosch water with 12 % and thereby also 12 % less NaCl will be consumed in the softener regeneration since less feed water will be taken up. The regeneration of the softener with RO brine instead of RO permeate did not yield tangible reduction in consumption of chemicals, since the savings in chemicals are too small to measure on a pilot scale. In terms of water usage, the savings are about 0.5 bed volumes, which is also not very significant.

2. Introduction

Fresh water is of major importance for the chemical industry, as it is used in many chemical processes. However, the continuous supply becomes more uncertain nowadays, as ground and surface water are depleting and getting less usable due to lower quality (i.e. becoming too saline). The reuse and production of industrial process water as well as turning to alternative sources of water delivers a sustainable solution to this problem. In this research the potential of new technology for demineralized water production from surface water and the reuse of the concentrate from RO for IX regeneration are investigated within the AquaSPICE project.

For the pilot tests the IMPROVED water treatment containerized pilots were used. These pilots were built within the IMPROVED project funded by Interreg Flanders-Netherlands. The IMPROVED pilots are housed in two 40 ft sea shipping containers and contain nine water treatment skids that can be rearranged in different configurations. They can treat up to two streams at the same time with nominal flow rate of 250 l/h each. The available water treatment skids are Reverse Osmosis (RO), Ultrafiltration (UF), Ion Exchange (IEX), Granular Activated Carbon (GAC), Electrodeionization (EDI), Electrodialysis with reversal possibility (EDR), Advanced Oxidation Processes (AOP), Membrane Aerated Bioreactor (MABR), and coagulation and flocculation including a lamella settler.

2.1 Problem Statement of the BASF Antwerp Case

BASF is one of the largest producer of base chemicals in the world. The site in Antwerp is the second largest BASF plant and it is dependent on surface water from the Netherlands (Biesbosch) to produce its demineralized water. This water source needs demineralization for use in steam-water cycles for energy production. A new demin plant was built in 2022 and is operated by Evides Industriewater which uses softener resins, double pass reverse osmosis and mixed bed (MB) polishing. Currently the softener is regenerated with a solution of NaCl and RO permeate - Figure 1.

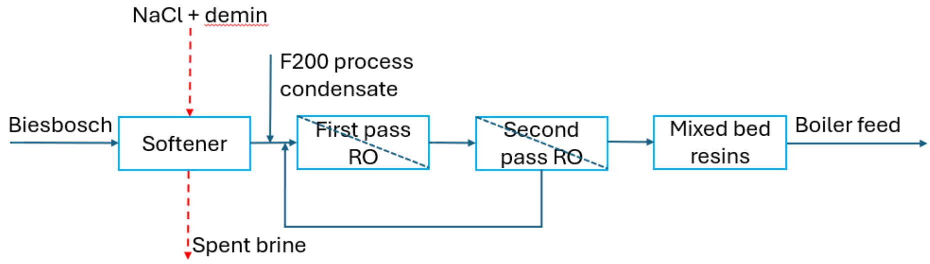

Figure 1 Simplified flow configuration at the new demin plant

The feed of the new demin plant is mainly Biesbosch water with a fraction of the F200 process condensate. The F200 is a condensate which has been in contact with the product and is therefore contaminated with organics but is not ionically loaded. The F200 is received at the new demin plant after activated carbon treatment.

With the AquaSPICE project, the BASF Antwerp plant strives to investigate and increase knowledge of cost-effective treatments for water reuse, concerning the reuse of RO concentrate from the new demineralized water production plant and the reuse of process condensate streams and process streams from the steam cracker plant for direct reuse or reuse after treatment. This report focuses only on the tests performed at the new demin plant. The targeted water quality after the second pass RO is <5 µS/cm, <2 ppm TDS and <50 ppb silica.

2.2 Goal

A new demineralized water production plant was commissioned in the summer of 2022 by Evides Industriewater at BASF. The Biesbosch water is already pretreated with coagulation ($FeCl_3$ dosage) and rapid sand filtration before entering the BASF Demin plant.

The objective is to investigate two options for increasing the water recovery of the demineralized water production plant and reducing scaling and biofouling on the membranes. Therefore, the feasibility of closed circuit RO (CCRO) for treating the RO concentrate will be investigated, in order to increase the water recovery - Figure 2. CCRO is a novel, patented RO configuration that is promoted to be less prone to scaling and biofouling on the RO membranes [1]. This technology was implemented inside the IMPROVED containers by UGent with exclusive permission from the patent holder DuPont. Therefore, the system is mimicking CCRO, but may not be completely identical to a regularly licensed system from DuPont.

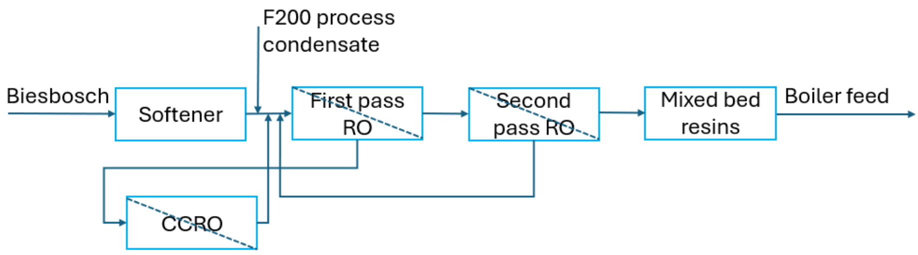

Figure 2 Possible implementation of the CCRO in the new demin plant of BASF by Evides

As a secondary goal, the reuse of the concentrated waste stream from the RO (Figure 3) will be investigated for regeneration of the softener resins in place of demin water. In this way less water and less salt will be used in the regeneration process as the RO brine is rich in NaCl and already softened. Thereby the overall water recovery can be increased (no use of the RO permeate for regeneration purposes and reducing brine discharges) and the chemical use decreased (less chemical cleaning of membranes needed).

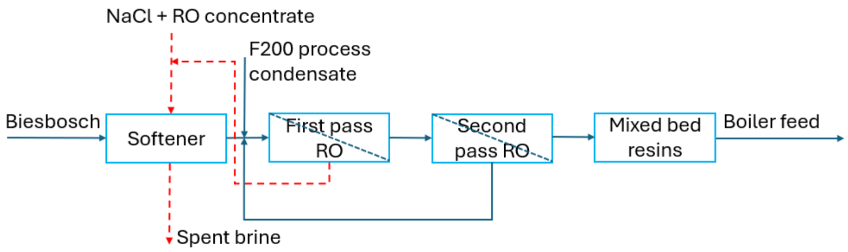

Figure 3 Current treatment train of the demin plant at E527. The reuse of the RO concentrate for softener regeneration is indicated with the red arrow.

The pilots were installed next to the demin plant of Evides Industriewater (E527), where the experiments were conducted in continuous mode taking the Biesbosch water and the RO concentrate from the demin plant.

3. Technologies of interest – theoretical background

3.1 Ion exchange

Ion exchange (IEX) is a process driven by electrochemical forces, where ions are removed from a solution by exchanging them with ions already attached to the functional groups of the IEX resin. In demineralization, the regenerated cation resins, including weak acid cation (WAC) and strong acid cation (SAC), have H^+ ions connected to their functional groups. Similarly, the regenerated anionic resins, such as strong base anion (SBA) and weak base anion (WBA), have OH^- ions or a free base attached, respectively. The degasser (DG) is responsible for removing CO2 after the cations are removed, which helps to reduce the bicarbonate load on the anion resin. The mixed bed (MB) column contains a mixture of SAC and SBA resins, and it serves to polish the water to achieve an electrical conductivity (EC) of less than < 0.1-0.2 µS/cm. As the IEX module continuously removes ions from the solution, the resin gradually becomes saturated, necessitating periodic regeneration. To monitor the effectiveness of the process, various parameters such as pressure, EC, pH, TOC, sodium (Na), and silica (Si) levels are measured before and after selected columns *Figure 4.*

In the case of softening, the cation resins (typically SAC) are regenerated with a concentrated sodium chloride solution, which results in the resin having Na^+ ions connected to its functional groups. As the hard water containing calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions passes through the softening resin, these ions are exchanged with the Na^+ ions on the resin, effectively removing the hardness from the water. The resin's capacity for softening gradually decreases as more Ca^{2+} and Mg^{2+} ions are exchanged, and eventually, regeneration is required to restore the resin's softening ability. Monitoring the hardness levels before and after the softening column helps to assess the performance of the softening process and determine when regeneration is necessary.

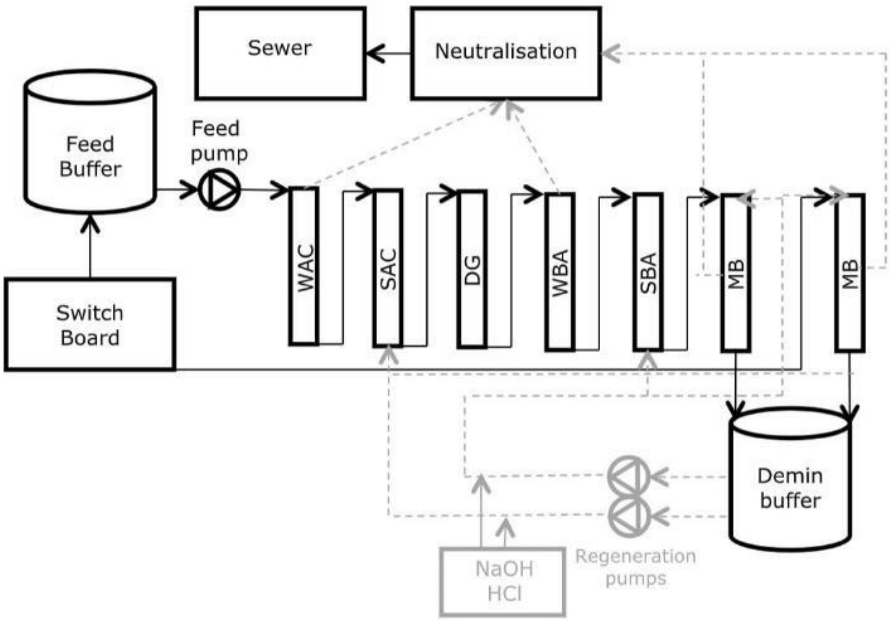

Figure 4 Schematic overview of the IEX module inside the IMPROVED containers. The gray routes are used during regeneration.

3.2 Reverse osmosis

Reverse osmosis (RO) is a membrane-based separation process that utilizes a pressure gradient to drive the separation of water and dissolved components through a semipermeable membrane. Unlike other membrane types, RO membranes are typically dense and do not have visible pores. The dense nature of the membrane allows for the mechanical rejection of suspended solids, while salts and water dissolve into the active layer of the membrane. The rejection of these dissolved components is primarily governed by the differences in their diffusion coefficients within the membrane matrix. Although membrane and solute charge also play a significant role in determining the rejection efficiency, a detailed discussion of these factors is beyond the scope of this report.

During the RO process, salts, suspended solids, viruses, and other dissolved components are retained in the concentrate stream, while water and some small dissolved components pass through the membrane and are collected in the permeate stream. Due to the nature of the RO process, the membranes are not typically cleaned by backwashing. Instead, they are subjected to clean-in-place (CIP) procedures or flushed with air to remove fouling and prevent clogging of the feed spacer. The feed spacer is a critical component in the RO system, as it helps to promote turbulence and reduce concentration polarization near the membrane surface - Figure 5.

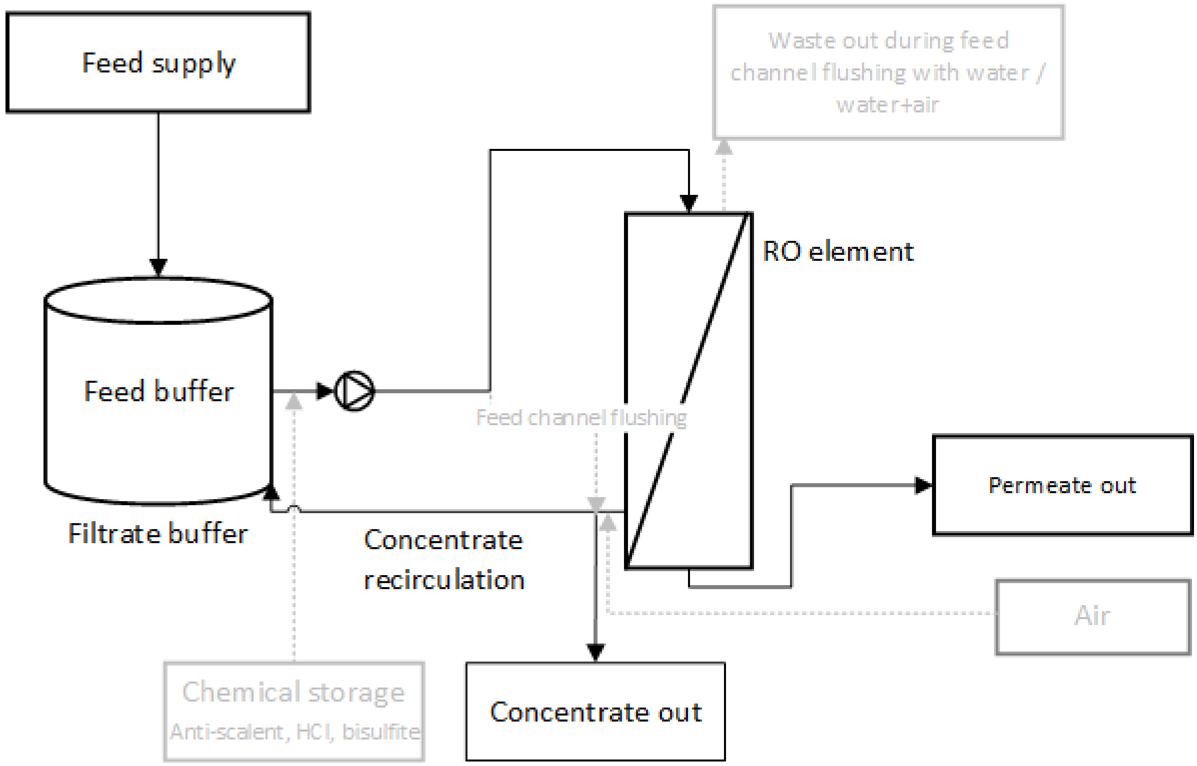

Figure 5 Schematic overview of the conventional RO module inside the IMPROVED containers. The gray routes are used during regeneration.

Closed circuit reverse osmosis (CCRO)

The closed-circuit reverse osmosis (CCRO) system operates in two distinct modes: closed-circuit desalination and flush cycle. During the closed-circuit desalination mode, the system recirculates the entire concentrate stream, which is blended with the raw feed, at high circulation rates. In this mode, no brine is produced, and the pressure within the system gradually increases as the osmotic pressure rises due to the accumulation of rejected salts (Figure 6). Once a predetermined filtration time elapses, the system transitions to the flush cycle, also known as the plug-flow mode. During this cycle, the concentrate valve opens, allowing the system to be flushed and the accumulated brine to be purged before crystals can form, thus preventing scaling [1] [2] [3] [4]. It should be noted however that if the crystallization kinetics are relatively quick (e.g. $CaCO_3$), the scaling may still occur.

The continuous fluctuation of hydraulic and osmotic pressure conditions in the CCRO system creates an unfavourable environment for microorganisms, effectively reducing the potential for membrane fouling. Moreover, the CCRO system achieves higher water recovery compared to conventional RO systems, which results in a decreased waste stream volume. However, it is important to note that the permeate quality may fluctuate during the concentration cycle, necessitating the use of a permeate buffer tank to ensure a consistent supply of high-quality water. One advantage of the CCRO system is its ability to operate at higher osmotic pressures than conventional RO systems. This allows for the treatment of feedwater with higher salinity levels, making it suitable for applications such as brackish water desalination or industrial wastewater treatment. Additionally, the periodic flushing of the system helps to maintain membrane performance and extend the membrane lifespan by reducing the accumulation of foulants and scalants. [1] [2] [3] [4].

The CCRO was implemented by modifying the conventional RO in the containers in accordance with the patent holder DuPont who allowed the modification exceptionally for UGent - Figure 6. The concentrate stream was directed to the feed of the pump instead of the buffer tank (Figure 5) and the programming was adjusted to accommodate the cyclic nature of CCRO. The water is recycled in the system for a set number of minutes and then the system will be flushed for a set time. The volumetric ratio of the filtration (closed loop) and flush cycle (open loop) dictates the recovery of the system. The volume flushed from the system was kept such that it matched or exceeded the dead volume of the system.

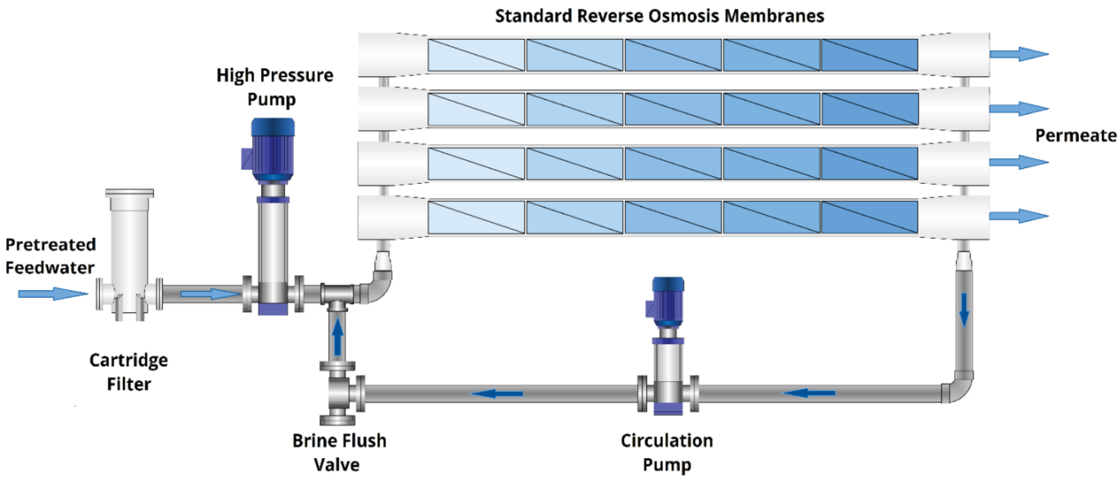

Figure 6 Schematic overview of the working principle of CCRO during closed circuit mode; after each filtration cycle the brine flush valve will open for certain amount of time [5]

4. Materials and Methods

4.1 Ion exchange

The deionization happens from top to bottom in vertical columns with 10 cm internal diameter, while the regeneration happens in the opposite direction. The normal hydraulic arrangement of the columns is WAC-SAC-Degasser-WBA-SBA-MB1 (Table 1). Mixed bed 2 (MB2) is a separate unit that can be connected to another technology.

During the trials at BASF only one column was filled with SAC resins (Dowex 650C). The water enters into the IEX softening unit, where divalent ions such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) from the feedwater are exchanged by sodium (Na^{+}). When the SAC resins reach an exhaustion point, in this case hardness breakthrough, it is regenerated with a concentrated sodium chloride solution, where the removed cations are replaced with Na^{+} ions. After setting a baseline with general NaCl regeneration, the regeneration will be done with the RO concentrate stream, with added NaCl (to reach the required concentration).

Table 1 Arrangement and resin type inside the IEX setup

Column	*Bed height, fresh (cm)*	*Resin*	*Column height (cm)*
SAC	*136 (10.6 L)*	*Dowex 650C (Na)*	*145*

To monitor the hardness after the softener, an ABI Hardness analyzer from Best Instruments B.V. was used – Figure 7

Figure 7 Hardness analyzer used after the softener

The device is fully automatic and uses a colorimetric titration method and the hardness is determined based on the intensity of the color. The device has different hardness operation ranges based on the reagent that is currently used, in our trials the 501/500 reagent was used that has a range of 0.53-5.34ppm total hardness as $CaCO_3$.

4.2 Reverse osmosis

In Figure 5 the scheme of the RO set-up is shown. The used RO membranes were a Dupont Filmtec LC HR-4040 and Dupont FilmTec BW30 PRO-4040, with an active membrane area of resp. 8.7 m² and 7.9 m². The LC HR was used until June 23rd and the BW30 PRO was used until the end of the tests. The pressure housing was a Codeline 40E100. The pH, flow, pressure, conductivity, temperature were continuously measured online with 10-seconds sampling intervals.

The main questions to answer with the tests for CCRO are: how stable is the RO performance in terms of scaling/fouling, what are the optimal operational settings (recovery, flux, (potential) antiscalant dosage) and what quality of CCRO permeate can be produced. Table 2 gives an overview of the CCRO tests on the RO concentrate of the demin plant.

Table 2 Planning of tests with CCRO

	Timeline	***Crossflow***	***Recovery***	***Flux***
Test 1	*27/3 - 5/4*	*1100 L/h*	*66%*	*20 Lmh*
Test 2	*5/4 – 12/4* *12/6-14/6*	*1100 L/h*	*66%*	*17 Lmh*
Test 3	*12/4 – 24/4* *6/6-9/6*	*1100 L/h*	*75%*	*17 Lmh*
Test 4	*24/4 – 4/6*	*1100 L/h*	*80%*	*17 Lmh*
Test 5	*16/6-18/6*	*1100 L/h*	*85%*	*17 Lmh*
Test 6	*23/6-3/7*	*1100 L/h*	*80%*	*15.5 Lmh*

5. Results and Discussion

Feed water quality

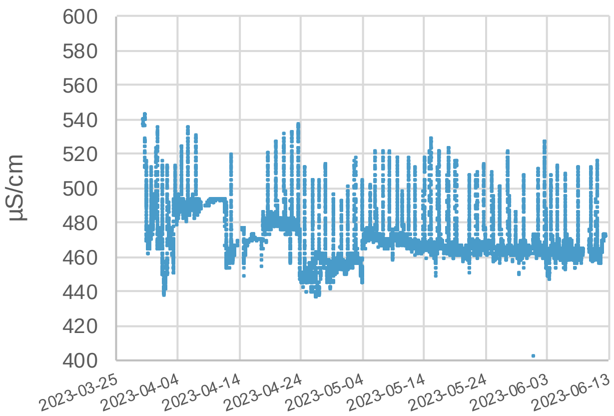

Figure 8 Conductivity of the Biesbosch feed

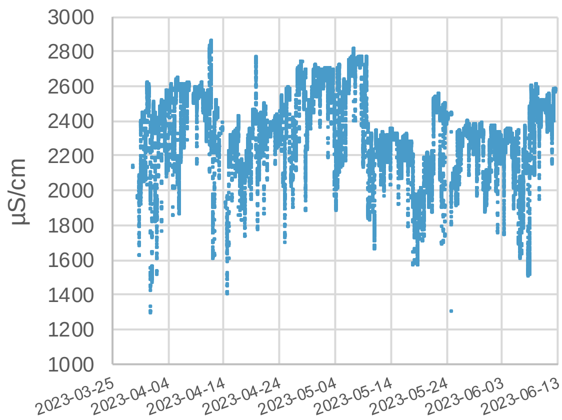

Figure 9 Conductivity of the RO concentrate feed coming from the demin plant of Evides

The quality of the Biesbosch water is relatively stable, and as can be seen in Figure 8, the conductivity baseline hardly fluctuates between 450 and 500 µS/cm. The spikes on the graph are artefacts due to the recirculation of the mixed beds of Evides during their startup.

The conductivity of the RO concentrate (Figure 9), coming from the first pass of the demin plant, fluctuates between 1700-2800 µS/cm. The quality of the RO concentrate in the pilot is dependent on the mixture of the demin plant's feed and the operational settings used. It should be noted that the SiO_2 in the incoming feed water from the new demin plant is quite high being 23.86 ppm. The fluctuations in conductivity are due to the feed being a mixture of Biesbosch flow at around 1000 m^3/h and the flow of the F200 process condensate. Overall, the process condensate can contribute for up to 30% of the feed depending on the availability, but mostly hovers around 10-20%. It should be noted that the F200 process condensate has a very low ionic load and contains mainly ammonia, organics and some iron, but exact analysis for this period is not available and it is highly variable in time.

Table 3 Average values of the quality of the feed water (Biesbosch and RO concentrate from the new demin plant)

Properties	Unit	Biesbosch			RO Concentrate (New demin)		
Number of samples		44			44		
		Average, stdev	Min	Max	Average, stdev	Min	Max
Conductivity	µs/cm	427 ± 20.3			2012.2 ± 272.5	1410	2550
pH		7.9 ± 0.3	6.3	8.3	8.2 ± 0.1	7.9	8.4
TOC	mg/L	3.0 ± 1.6	1.6	8.2	15.1 ± 5.6		
Br - Bromine	mg/L	0.1 ± 0.1	0.1	0.4	0.6 ± 0.1	0.3	0.9
Ca - Calcium	mg/L	42.8 ± 9.1	7.5	51.9	0.4 ± 0.3	0.1	1.6
Cl - Chloride	mg/L	53.5 ± 21.6	31.1	183.9	245.5 ± 35.7	142.9	319.4
Cr - Chromium	µg/L	<0.8	0.8	0.8	0.9 ± 0.4	0.8	2.9
Cu - Copper	µg/L	1.1 ± 0.3	0.1	2.4	3.7 ± 1.8	1	7
Fe - Iron	µg/L	36.5 ± 23.9	23.9	174.5	117.7 ± 92.9	58	563.7
Fl - Fluoride	mg/L	0.2 ± 0.1	0.1	0.8	1.1 ± 0.2	0.7	1.5
K - Potassium	mg/L	7.5 ± 4.6	4.2	35.4	23.2 ± 6.8	12.8	44.7
Mg - Magnesium	mg/L	6.1 ± 1.6	0.7	7.4	0.1 ± 0.1	0.02	0.8

Na - Sodium	mg/L	41.9 ± 13.9	29.3	94.5	513.7 ± 74.0	369.0	649.0
NH_3 - Ammonia	mg/L	1.1 ± 4.0	0.1	18.8	1.1 ± 0.7	0.1	4.7
Ni - Nickel	µg/L	1.8 ± 1.2	1	6	8.4 ± 4.1	1	17
NO_2 - Nitrogen dioxide	mg/L	0.2 ± 0.1	0.1	0.5	0.10 ± 0	0.1	0.2
NO_3 - Nitrate	mg/L	10.8 ± 3.3	8.7	30.2	48.4±8.2	30.2	61.7
PO_4 - Phosphate	µg/L	18.4 ± 34.6	10	203	18.3±34.7	10	205
SiO_2 -Silicon dioxide	mg/L	5.0 ± 0.5	4.1	6.2	23.9±3.6	15.5	30.5
SO_4 - Sulphate	mg/L	45.1 ± 2.9	31.7	50.2	248.9±35.2	145.1	316.0
Zn- Zinc	µg/L	8.3 ± 10.7	2.5	62.7	22.1±17.7	9.6	101.9

Performance of CCRO

Permeate quality

Different operational settings (flux, recovery, filtration time, flush time) have been tested with the CCRO within a few months of testing, an overview is given in Table 2. The average quality of the CCRO permeate can be seen in Table 4. Mainly chloride was found in the permeate water, also some sodium, nitrate and sulphate - Table 4.

Table 4 Lab results RO permeate

Properties	Unit	CCRO		
Number of samples		44		
		Average, stdev	Min	Max
Conductivity	µS/cm	185.0 ± 167.8	45.6	1007
pH		7.2 ± 0.4	6.4	8.0
TOC	mg/L	0.7 ± 0.6	0.0	2.3
Br - Bromine	mg/L	0.1 ± 0.0	0.0	0.2
Ca - Calcium	mg/L	0.1 ± 0.1	0.0	0.6
Cl - Chloride	mg/L	20.1 ± 12.6	6.6	55.3
Cr - Chromium	µg/L	0.8 ± 0.0	0.8	0.8
Cu - Copper	µg/L	1.0 ± 0.0	1.0	1.2
Fe - Iron	µg/L	7.6 ± 7.6	1.0	46.1
Fl - Fluoride	mg/L	0.1 ± 0.0	0.1	0.2
K - Potassium	mg/L	2.4 ± 2.5	0.6	16.2
Mg - Magnesium	mg/L	0.0 ± 0.0	0.0	0.1
Na - Sodium	mg/L	44.3 ± 44.7	12.9	276.4
NH_3 - Ammonia	mg/L	0.7 ± 0.9	0.1	5.8
Ni - Nickel	µg/L	1.1 ± 0.5	1.0	4.0
NO_2 - Nitrogen dioxide	mg/L	<0.1 ± 0.0	0.1	0.1
NO_3 - Nitrate	mg/L	10.7 ± 4.7	0.1	21.3
PO_4 - Phosphate	µg/L	19.6 ± 38.0	10.0	209.0
SiO_2 -Silicon dioxide	mg/L	1.7 ± 1.4	0.4	5.3
SO_4 - Sulphate	mg/L	11.4 ± 12.6	0.1	46.9
Zn - Zinc	µg/L	3.4 ± 8.0	1.0	38.2

The performance of the CCRO in terms of permeate quality is visualized in the following graphs (Figure 10, Figure 11, Figure 12). The changes in operational settings are indicated with the vertical lines and comments.

As can be seen there is high variation in the salt passage (Figure 12), resulting in fluctuating permeate quality both in terms of TOC and conductivity, although the TOC variation is much higher. The permeate quality was excellent (TOC 60 ppb, 50-80 µS/cm) at the start, when running at a recovery of 66% and flux of 17-20 Lmh. The recovery was increased to 75% after two weeks, and the conductivity and TOC started to increase. However when changing the recovery to 80 %, the permeate quality worsened even more, fluctuating up to 3 ppm TOC and 400 µS/cm conductivity. The salt passage increased to 5%, and the membrane was replaced as membrane damage was suspected. The permeate quality and RO performance improved somewhat, but it was still fluctuating although no obvious difference in the feed water was seen. The o-rings on the permeate collection tube were also inspected and replaced without any improvement in permeate quality.

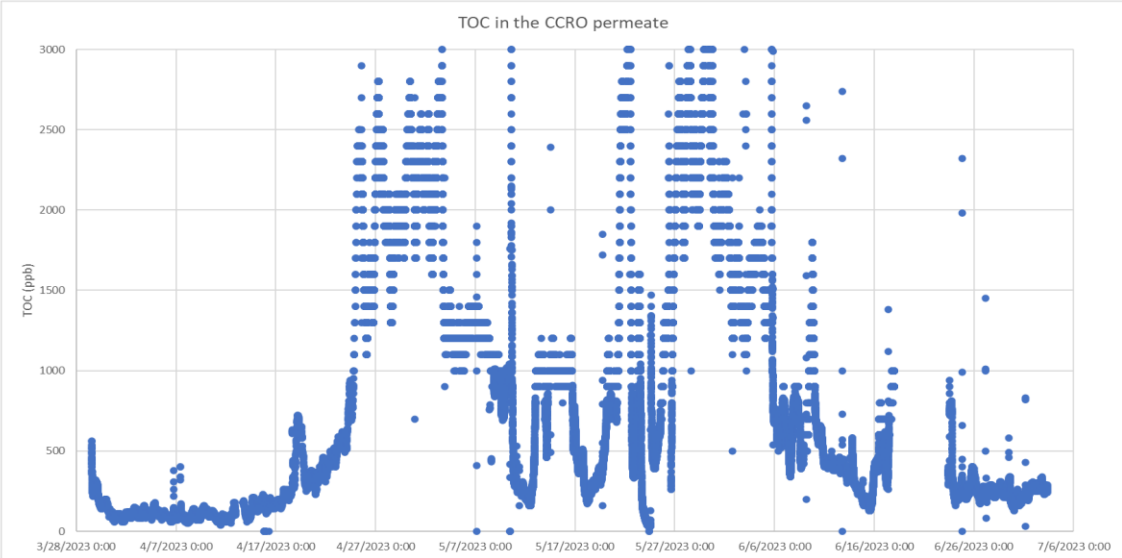

Figure 10 TOC in the CCRO permeate

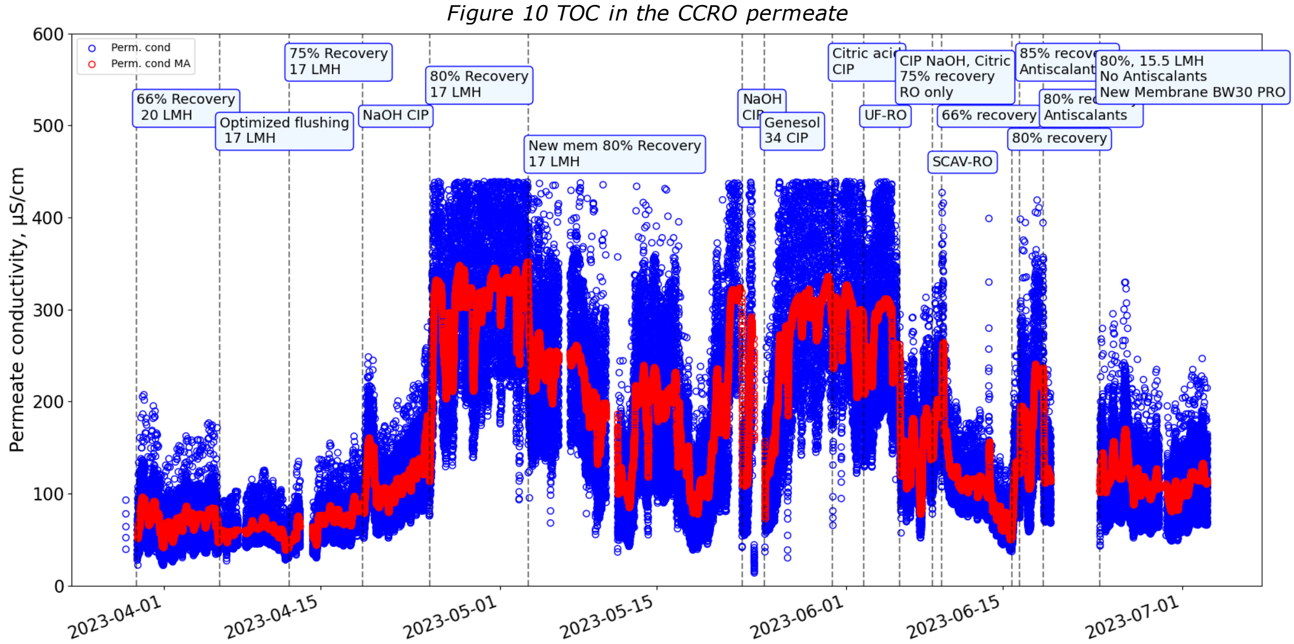

Figure 11 Permeate conductivity of CCRO permeate, moving average in red. It has to be noted that at times the maximum conductivity of the probe of the permeate was reached at around 450 µS/cm

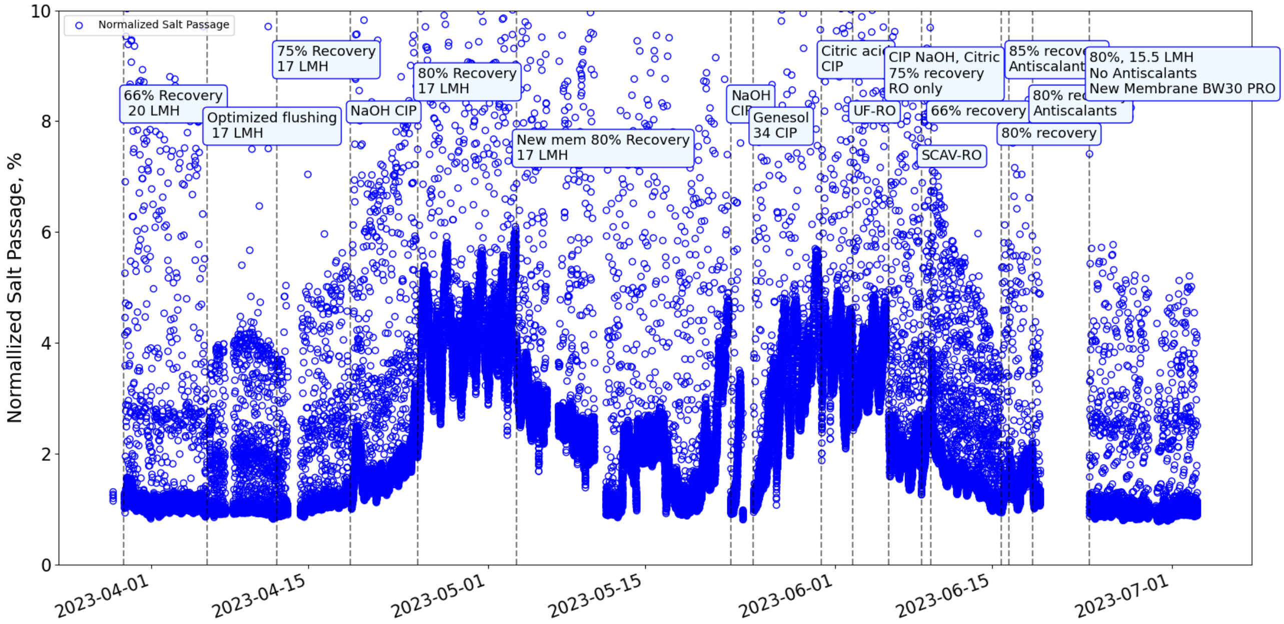

Figure 12 Normalized Salt Passage during CCRO tests

Several CIPs with different chemicals were performed: sodium hydroxide at pH 12, Genesol 34 at pH 12, and citric acid at pH 2. Genesol 34 is a commercial RO cleaner used at 3% concentration and high pH that is claimed by the manufacturer to be a strong Fe cleaner. After a CIP, the salt passage seemed good (around 1%, Figure 13) for about 6 hours, after which it increased again to 3% indicating a fouling-related problem. It should also be noted that the RO works with recirculation, so it also takes some time until the concentration in the loop stabilizes after CIP, but the normalization of the salt passage should exclude this effect. Also, the dead volume of this loop is around 6-7L, so after 1 or 2 cycles (10-20 min each, seen as a vertically inclined line on Figure 13), it should be completely stable.

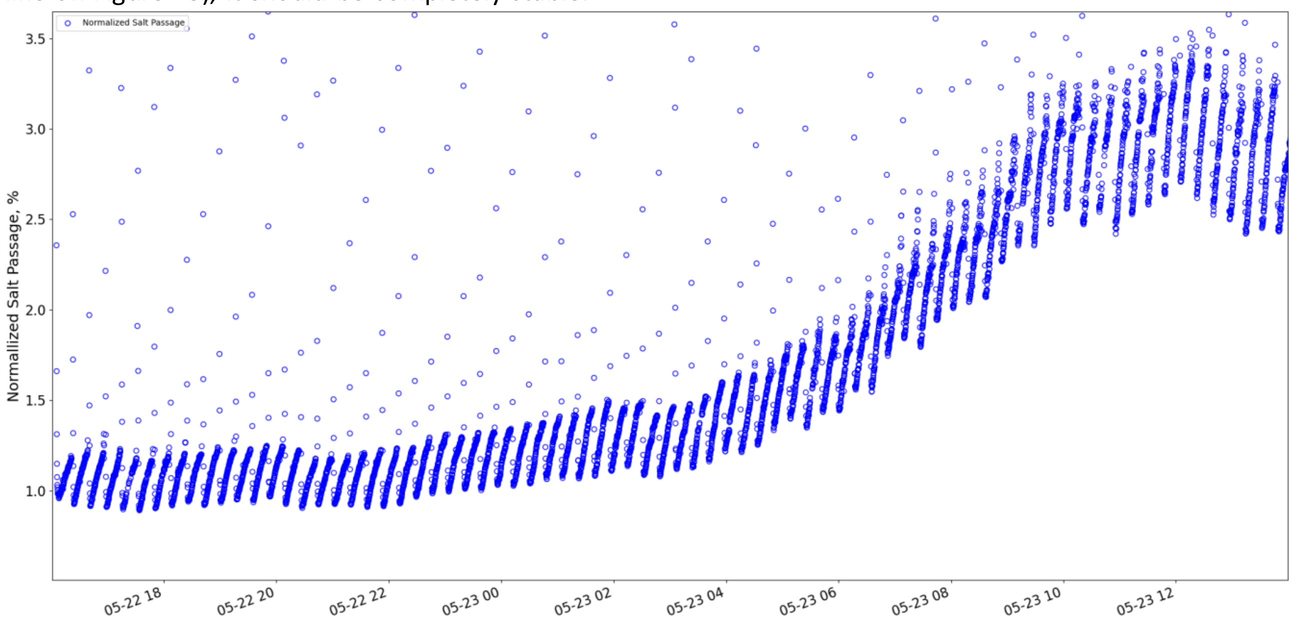

Figure 13 Increasing normalized salt passage after CIP with NaOH. Horizontal axis markers every 2 hours.

In order to investigate the problem with the poor rejection of the CCRO, several things were tested towards the end of the testing period as seen in Figure 14 and Figure 15:

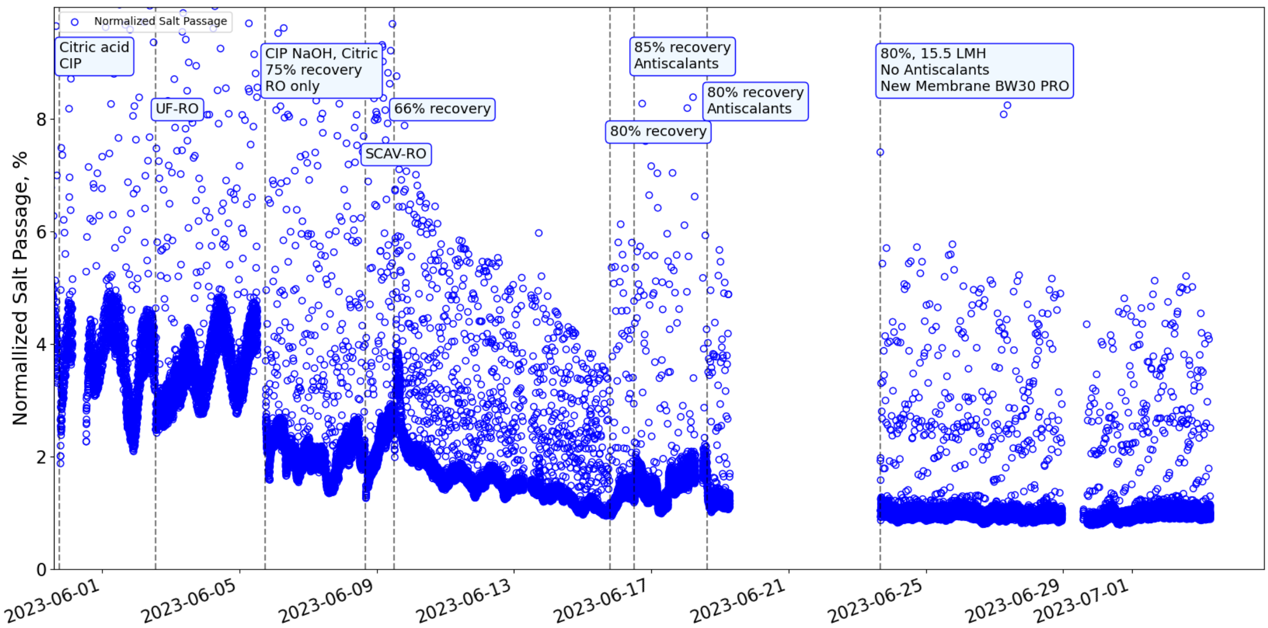

Figure 14 Zoomed in graph on the normalized salt passage

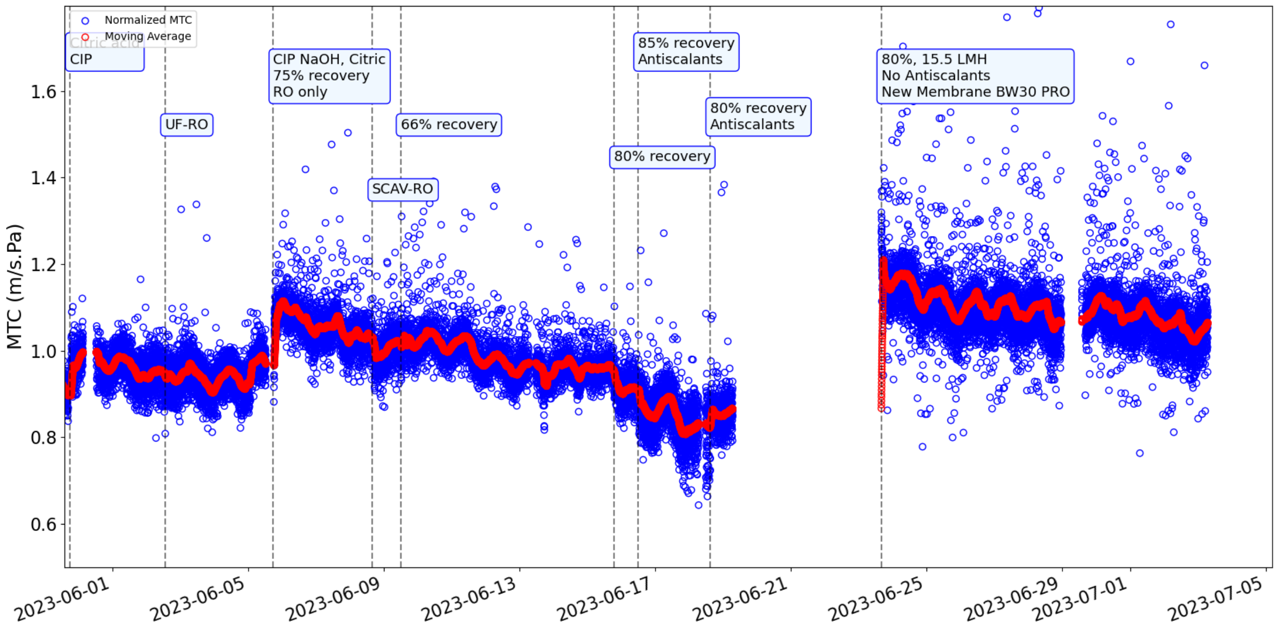

Figure 15 Zoomed in graph on the normalized mass transfer coefficient

UF was placed before the RO with no effect on the normalized salt passage or the MTC. The UF would normally sieve out dead cells and to some extent humic acids with nominal pore size of 20 nm. Similarly, a scavenger resin (SCAV) was placed before the RO with little effect on the salt passage and was subsequently removed. When the recovery was reduced from 80 to 75%, the normalized salt passage significantly reduced from 3% to around 1%. Therefore, it seems like the recovery plays a significant role in the rejection of the RO. After this the recovery was increased back to 80% to induce fouling followed by increase of recovery to 85% together with antiscalant. The antiscalant used was Cosun Carboxiline 25-30 up to 5 ppm concentration. The antiscalant was dosed mainly for its dispersive qualities so that a possible cake-layer formation is prevented. It seems like the antiscalant dosing helped with the permeate quality, especially at 80% recovery. Finally, a new membrane was installed and operated at 15.5 LMH and 80% recovery and this produced very good quality permeate in comparison to the rest of the tests.

It is suspected that the worsening permeate quality is due to cake-enhanced concentration polarization - Figure 16.

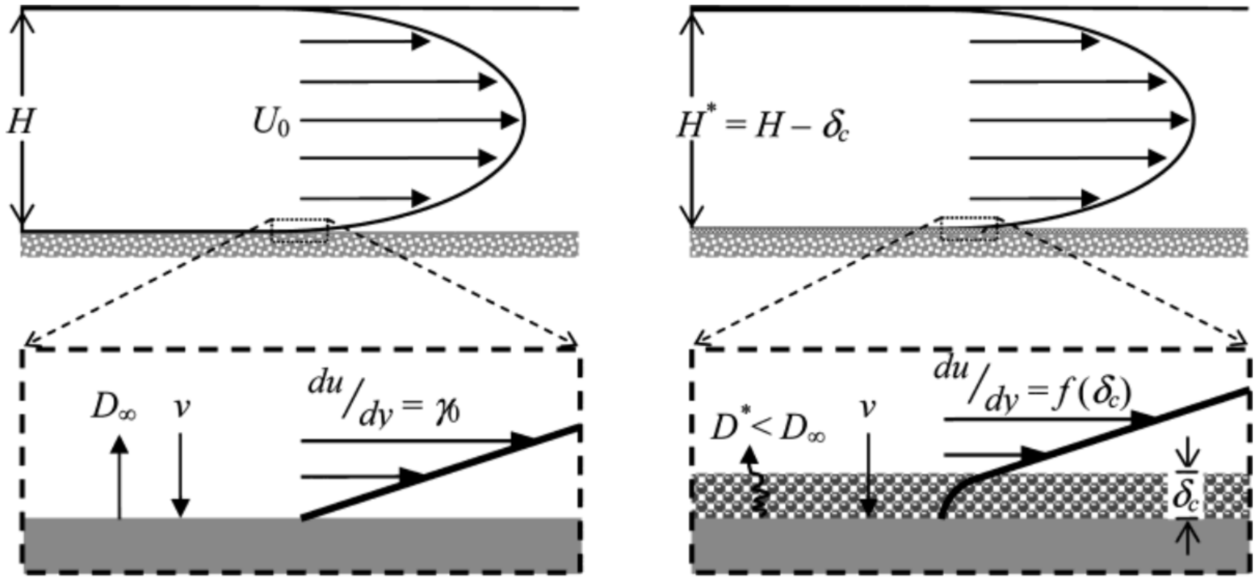

Figure 16 Cake-enhanced concentration polarization conceptualized by Hoek et. al. [6]. Clean membrane on the left side and cake-enhanced polarization on the right side.

In cross-flow membrane filtration, the complex interplay of physicochemical factors contributes to the formation of cake-enhanced concentration polarization. The bulk tangential flow velocity (U0) plays a crucial role in determining the wall shear rate (γ0), which, in combination with the ionic diffusion coefficient, governs the mass transfer within the salt concentration polarization layer. As the colloid deposit layer hinders both tangential flow and ion back-diffusion, it amplifies the ionic concentration at the membrane surface, consequently increasing the trans-membrane osmotic pressure. The diagram illustrates these phenomena using various parameters: D represents the diffusion coefficient, with D_∞ and D^* denoting the bulk and hindered values, respectively; v and u signify the local permeate and tangential flow velocities; H indicates the cross-flow filter channel height; δc represents the cake thickness; and H^* corresponds to the effective fouled channel height resulting from the cake layer formation [6].

It is stated that salt passage can increase up to 5% by the development of a cake layer of dead cells and particles, causing cake enhanced concentration polarization. The enhanced concentration polarization phenomenon is attributed to the reduced back-diffusion of salts and other compounds through the cake layer [7]. The concentration of salts close to the membrane interface increases, resulting in a worse permeate quality. The cake enhanced polarization can happen in seconds, explaining the high salt passage with the new membrane and a few hours after a CIP. The expectation is that the cake is formed by an interaction between silica and humic acids [8] (both present in the Biesbosch water).

An additional test was performed to see the change in salt passage for several recoveries: resp. 66%, 75%, 80% and 85%. Figure 17 shows that the salt passage increases instantaneously with the increasing recoveries. Also the MTC decreases clearly for every recovery (Figure 18). By returning to 66% recovery, the salt passage decreases and MTC increases again. This again suggests that a reversible cake-layer is forming on the membrane and falls in line with the cake-enhanced concentration polarization theory.

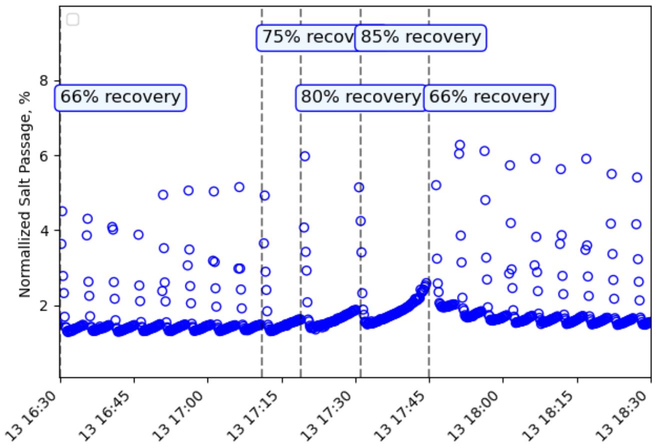

Figure 17 Normalized salt passage for several recoveries. Horizontal axis markers every 15 minutes.

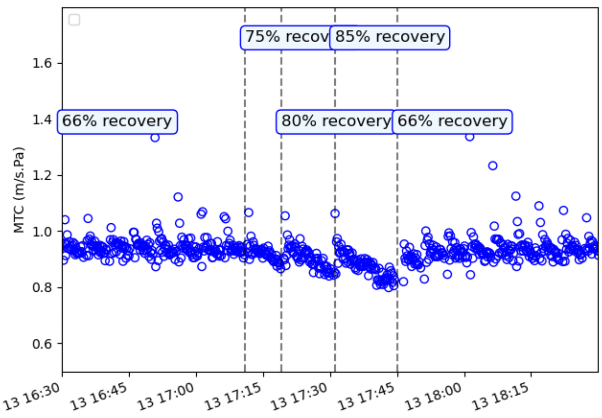

Figure 18 Normalized MTC for several recoveries. Horizontal axis markers every 15 minutes.

Fouling and cleaning

In general, the membrane was recovered best with a basic CIP with air flushes, in order to detach the cake layer from the membrane. In air flush mode 1.5 bar compressed air is injected after the high pressure pump in a forward flush mode and the membrane feed channel is flushed with a mixture of water and air bubbles. The fact that basic CIP recovers the membrane best suggests fouling of biological or organic nature. The average CIP frequency was once every two weeks, but probably this can be optimized by adjusting the operational settings. The CIP does not recover the membrane to new state, but this is not expected. What we do see is that the basic CIPs recover the membrane consistently to a level of 1.0-1.1 MTC, while for a new membrane it is 1.3. In the period 22/5 to 5/6 several CIPs were done in order to find the optimal protocol and the CIP with NaOH followed by citric acid seemed to be the most effective in restoring the normalized MTC and the normalized pressure drop (NPD Figure 20 Normalized pressure drop during CCRO tests).

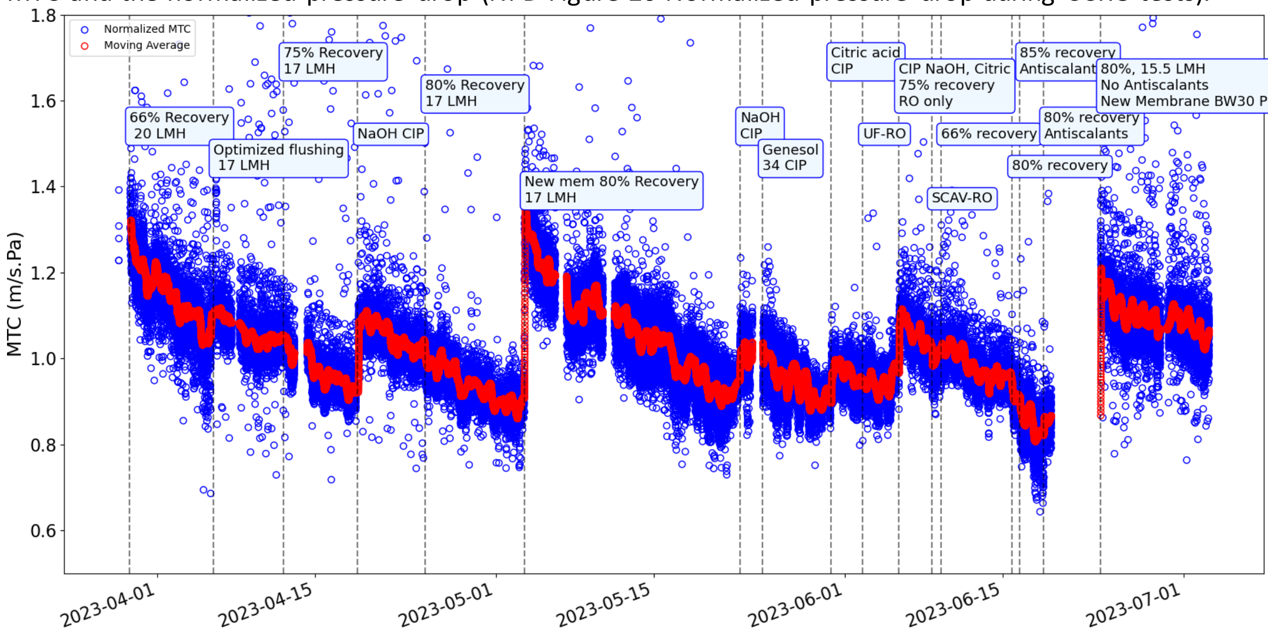

Figure 19 Normalized mass transfer coefficient during CCRO tests

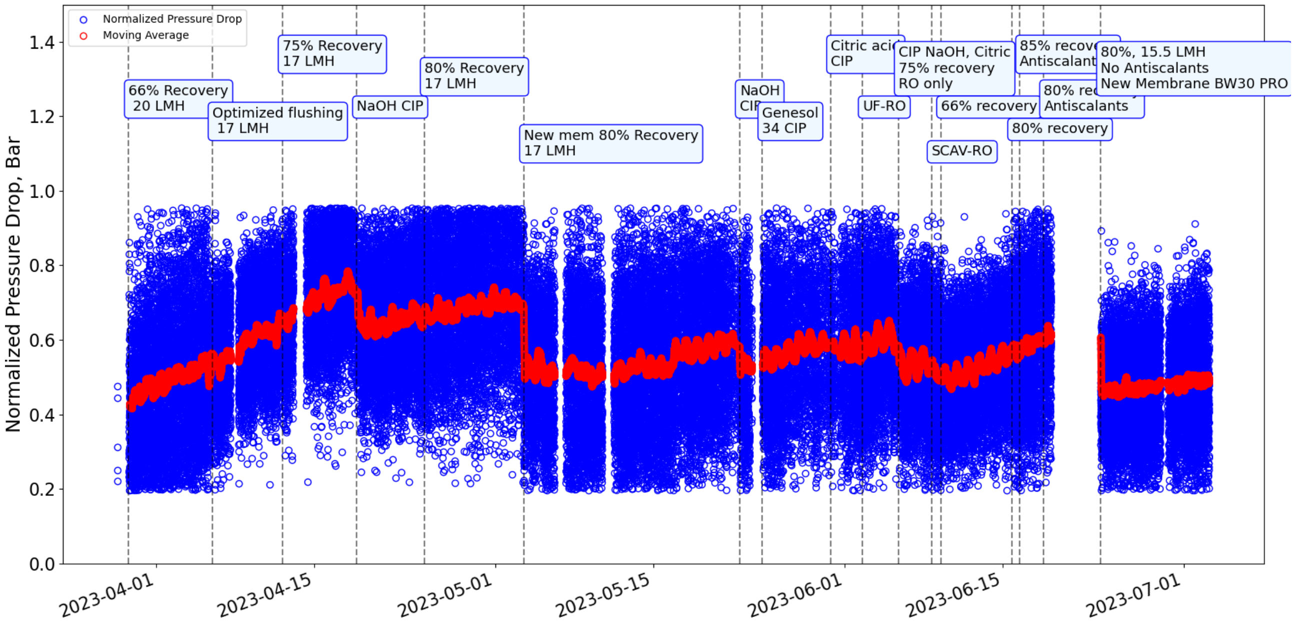

Figure 20 Normalized pressure drop during CCRO tests

The membrane replaced on 06/23 was examined with membrane autopsy, and the predominant elements found during the analysis are shown in Figure 21. It should be stated that the concentrations of the ions are no absolute values as the sample was not taken for a well-defined membrane area. Images of the fouling on the membrane can be found in Appendix 1. The element found in the largest quantity was silica, which is probably coming from the sand filtration of the Biesbosch water. We expect that this silica is colloidal of nature as opposed to an impermeable glassy layer, since the fouling on the membrane was largely reversible. The silica in the Evides RO concentrate entering the pilots has an average concentration of 23.9 ppm in the feed and after 80-85% water recovery in the CCRO, the solubility limit is probably exceeded towards the end of the concentration cycle. The second most common element was Fe which is probably residual iron from the coagulation of the Biesbosch water before the sand filtration. When the water is concentrated in the CCRO the organics are coagulating with the residual iron. Severe classic scaling of Ca or Mg was not noticed, even though no antiscalant was dosed for the majority of the experiments which is also expected as the water is softened before the RO in the new demin plant.

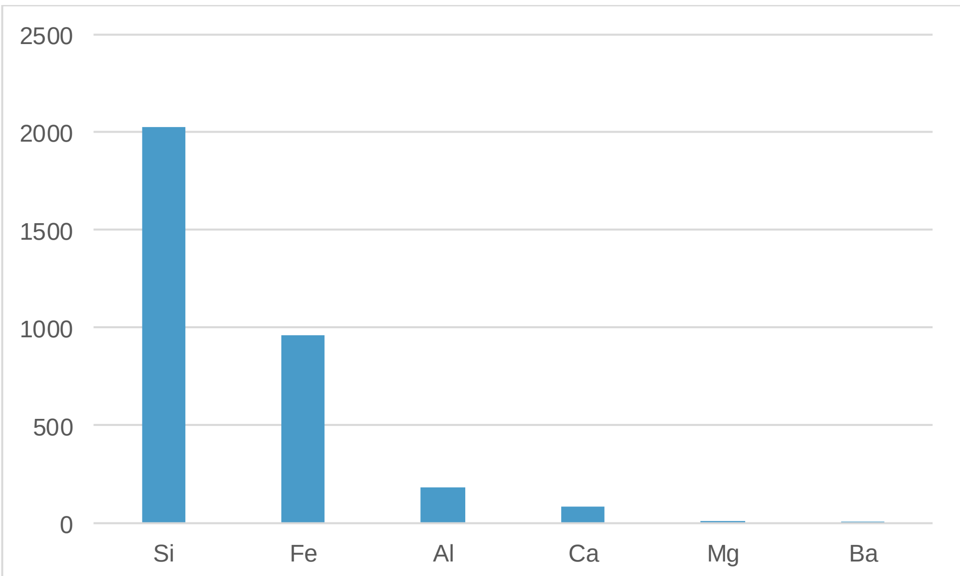

Figure 21 Elements found on the membrane during the autopsy, ppm

Additionally several samples from the CIPs were also taken during the operation Table 5.

Table 5 Elements observed in the cleaning solution during CIP

Date	Method	TOC mg/L	Fe mg/L	Cu mg/L	SiO2 mg/L	Mn mg/L	Pb mg/L	Sr mg/L
30-May	Genesol 34	33.500	7.6	1.57	0.02	0.10	0.07	0.2
05-Jun	Citric pH 2.5	29.400	6.3	1.02	< 0.01	< 0.05	0.05	< 0.1
05-Jun	NaOH pH12	1.210	3.0	0.06	0.41	< 0.05	< 0.05	0.2

The cleaning with citric and NaOH was performed immediately one after the other in that order. All of the cleaning methods show large concentrations of TOC, but it should be noted that the majority of the organics with the citric acid and the Genesol 34 solution are due to the cleaning solution itself. Overall, the citric acid and the Genesol are effective in removing Fe and Cu, but only the NaOH removes some silica as well that is probably bound to biological fouling. It should be noted that the NaOH also removes some iron, which is also probably bound to organics which are dissolved with the base.

Summary CCRO

The operation of the CCRO was stable in terms of pressure but was varying quite a lot in terms of permeate quality. It should be noted that even with the bad permeate quality, the values are better than the feed water of the new demin plant and it should be feasible to reuse the produced water by blending it with the Biesbosch water. However, probably the quality of the CCRO permeate is not sufficient to send it directly to the second pass of the RO in the new demin plant.

We noticed several things that improve the permeate quality: 1) reduction of the recovery 2) addition of antiscalants to disperse the cake layer which would also help with the silica and iron scaling 3) reduction of the flux. Overall, the most feasible route is to reduce the flux to 15.5 or lower. By reducing the flux of the CCRO to 15.5 lmh and 80% recovery the permeate quality and operational pressures remain very good. The salt passage was around 1%, resulting in permeate quality of 100-150 μS/cm and 200-300 ppb TOC. During the last week of operation, the NPD was stable and MTC was decreasing relatively slow. While the antiscalants are not strictly needed for the Ca and Mg, they may help with the silica and iron scaling while also reducing the effect of cake-enhanced concentration polarization.

If the CCRO is implemented at 80% recovery, the overall recovery of the plant will increase from 85 to 97 %. This will allow BASF and Evides to save 12% on NaCl for the regeneration of the softener as 12 % less feed water will be used. In fact, the NaCl savings may be even larger as the feed water is a mixture of Biesbosch and on average 10-15% F200 process condensate, hence the percentage of water going over the softener will be further reduced - Figure 2.

Performance of softener regeneration with RO concentrate

During the preliminary lab experiments, the regeneration of the softener was not successful with the RO concentrate, since most of the calcium and magnesium was released with the conventional NaCl regeneration, after the RO concentrate regeneration [9]. It was concluded that the concentration of monovalent ions in the concentrate was not high enough to have a sufficient driving force to perform the regeneration. This was confirmed by the results of a separate pilot study from Evides Industriewater, where salt needed to be added for the softener regeneration with RO concentrate.

Overall then the strategy was to use RO concentrate instead of demin in the regeneration process, thus saving water with negligeable saving on chemicals.

The pilot experiment was started by creating a baseline with normal regeneration (demineralized water + NaCl). Therefore, the aim was to have comparable regeneration settings as the Evides demin plant. After a few weeks on June 9th, RO concentrate from the demin plant and NaCl were used to regenerate the softener instead of demineralized water. The used operational settings are given in Table 6.

Table 6 Operational settings baseline and with RO concentrate regeneration

Flowrate (l/h)	Max. Hardness (ppb)	Dosing chemicals (min)	NaCl 9% solution (l)	NaCl (g/L resin)	NaCl (g)
250	2000	11	2.5	81	890

The performance of the softener with demin water and with RO concentrate can be seen in Figure 22 - Figure 25.

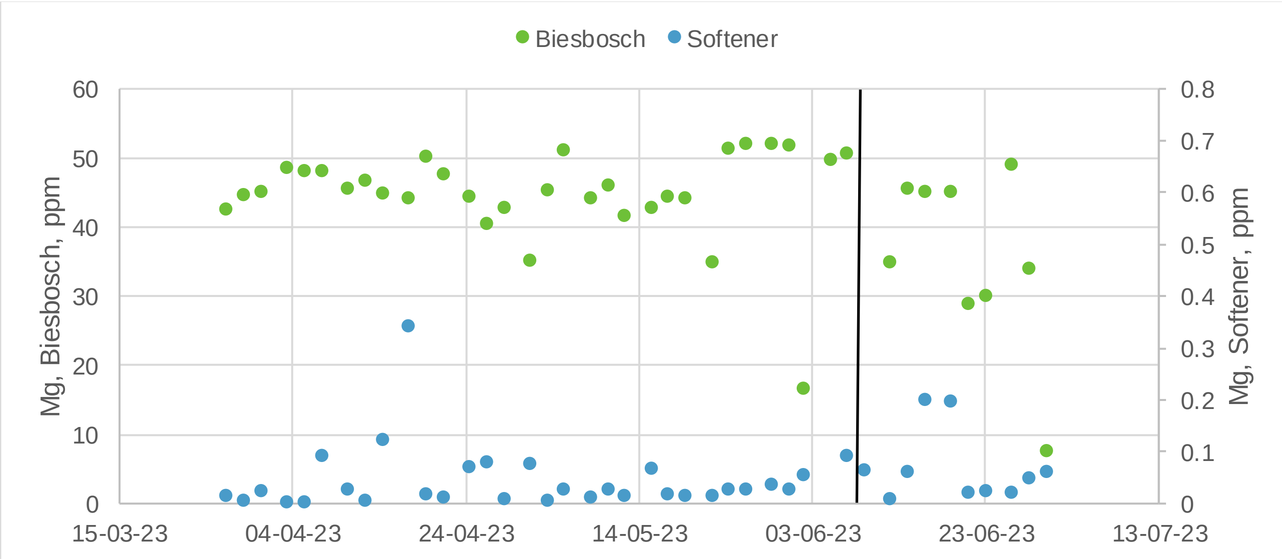

Figure 22 Magnesium before and after softener, ppm. The vertical line denotes the switch from demin to RO concentrate.

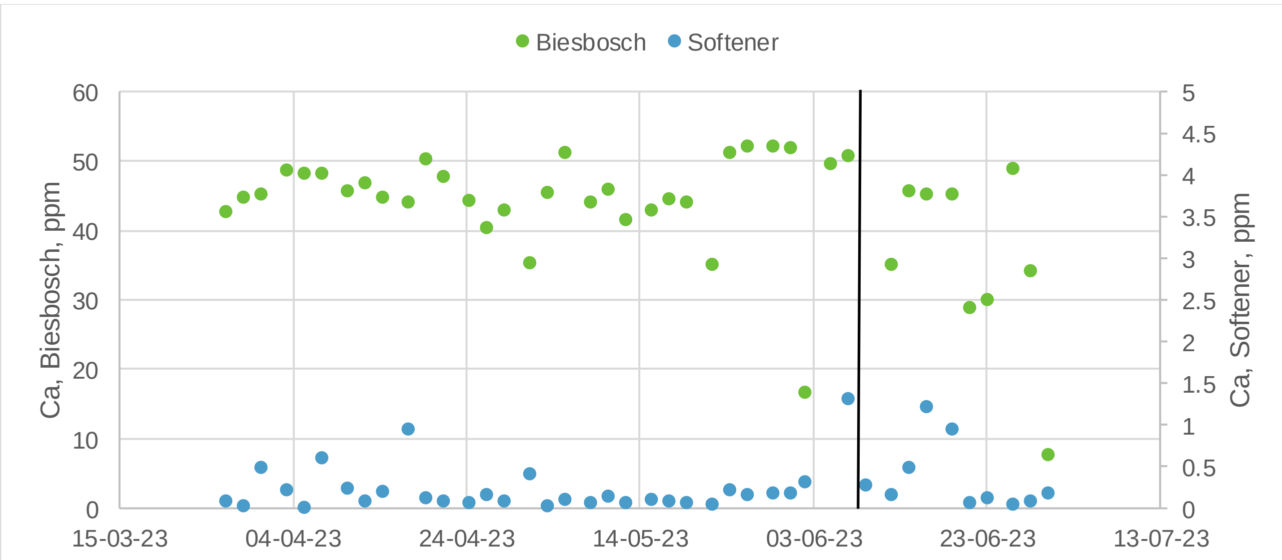

Figure 23 Calcium before and after softener, ppm. The vertical line denotes the switch from demin to RO concentrate.

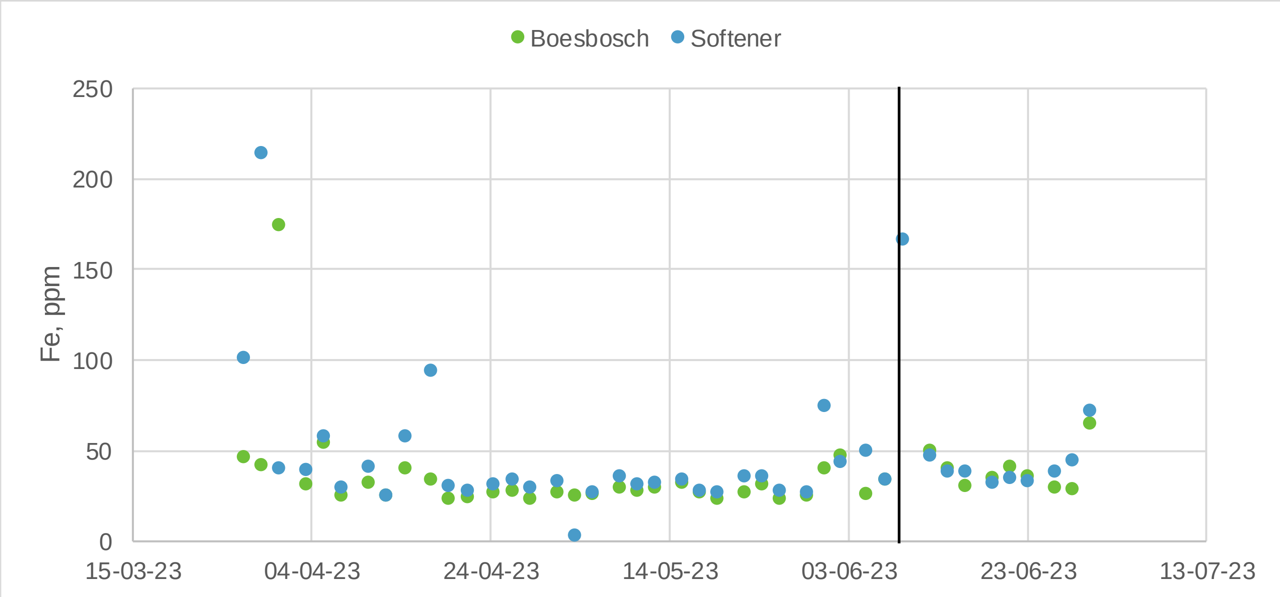

Figure 24 Iron before and after the softener, ppb. The vertical line denotes the switch from demin to RO concentrate.

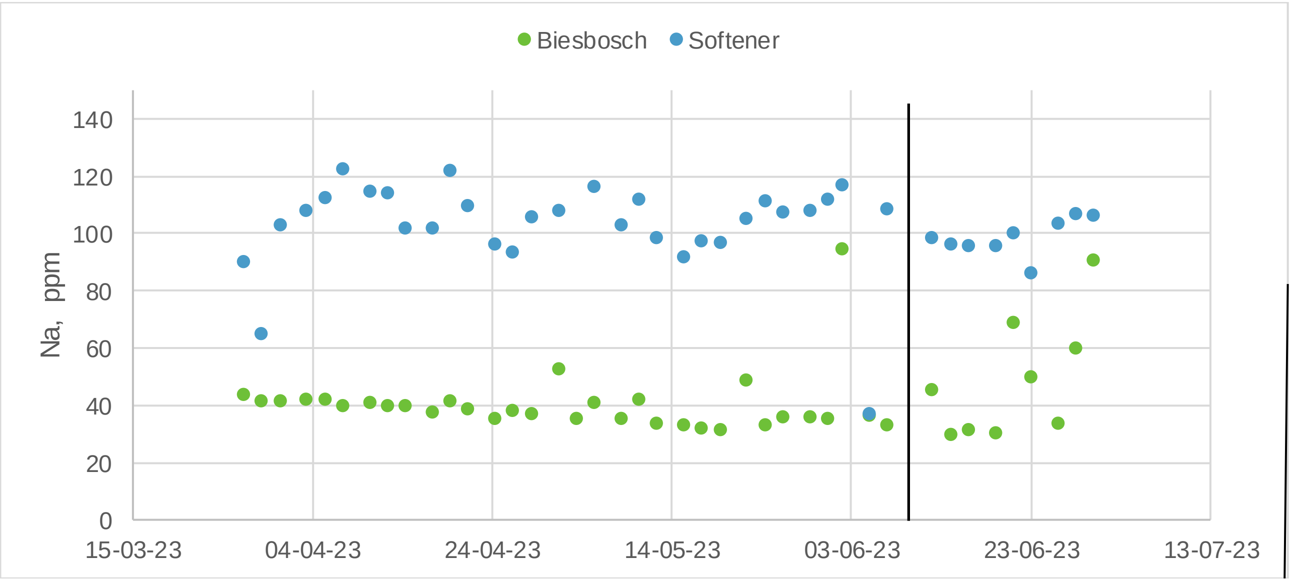

Figure 25 Sodium before and after softener, ppm. The vertical line denotes the switch from demin to RO concentrate.

From the results, there is no significant difference in the performance of the softener with demin or RO concentrate in terms of quality, although these tests are quite short. Longer tests are needed to prove that scaling is not occurring as the Ca and the Mg can react with anions from the concentrate. Calcium and magnesium are well removed by the softener and exchanged for sodium, however iron is not well removed. This is probably due to the very low starting concentration of the iron in the water. The water saved by using RO concentrate instead of demin is about 5 liters or 0.5 bed volumes (11 minutes at 27 l/h).

An attempt was made to measure the reduction in chemical usage with the new regeneration method. However, it was very hard to obtain a stable operation of the system due to a problems with integration of the hardness analyzer, inconsistencies with RO brine concentration (solved with installation of a stirrer in the brine tank), inconsistent dosing pump operation due to blockage with salt granules and others. The chemical savings are expected to be negligeable as the Na in the RO concentrate is 514 ppm (Table 3) while the softener is typically regenerated with ~10 % NaCl or 100 000 ppm NaCl or ~40 000 ppm Na. Therefore, the estimated savings on NaCl are less than 1.5%.

One could argue that instead of the RO concentrate from the new demin plant, the CCRO concentrate can be used which would be ~5x more concentrated, leading to more significant savings in chemicals. However, the RO concentrate contains anions such as SO_4^{2-}, HCO_3^- and CO_3^{2-}, which under the right conditions, can precipitate with the Ca^{2+} and Mg^{2+} cations that are being released from the SAC resin bed during the regeneration. Hence, caution should be taken out especially for the irreversible scaling formed by $CaSO_4$.

Further water and chemical savings can be done if the resins are continuously regenerated with RO concentrate, i.e. two softeners, one in regeneration and one in operation but this was not possible to test in the containers. In this case the monovalent ions have more time to react with the resins and exchange for hardness and ultimately the chemical regeneration may need to happen with less NaCl. However, this configuration involves building an additional softener (in case one doesn't already exist), imposing much larger CAPEX requirements in case a retrofit is needed.

For newly built systems, implementing this regeneration route appears to be feasible. The savings may not be substantial, but the required changes to the infrastructure are also minimal. In contrast, retrofitting this regeneration process into existing systems is likely not cost effective.

6. Conclusions

A system mimicking Closed Circuit Reverse Osmosis (CCRO) was implemented inside the IMPROVED containers of UGent and was used to treat the RO concentrate of the new demineralization (demin) plant at BASF. The operation of the mimic CCRO system showed stable pressure levels, but the permeate quality fluctuated depending on operational settings. The issues with varying permeate quality were attributed to cake-enhanced concentration polarization caused by colloidal silica and organics coagulated with iron. Despite the poor quality of the permeate, it was still superior to the feed water for the new demin plant, suggesting the potential for the reuse of produced water by blending it with Biesbosch water. However, the CCRO permeate will likely have to be reused in the first pass instead of the second pass of the new demin plant.

Improvements in permeate quality were observed with the reduction of recovery rates, the addition of antiscalants, and a decrease in flux. The most effective approach appeared to be lowering the flux to 15.5 L/m^2h (lmh) and maintaining a recovery rate of 80 %, which ensured excellent permeate quality and operational pressures. With this setting, the permeate showed a salt passage of about 1 %, with 100-150 µS/cm conductivity and 200-300 ppb TOC.

By operating the CCRO at 80 % recovery, the overall recovery rate of the plant could be increased from 85 % to 97 %, also allowing for significant savings in sodium chloride (NaCl) used for softener regeneration due to a 12 % reduction in feed water intake.

During the trials the reuse of RO concentrate instead of demin water for the regeneration of softener was also tested. The implementation of this should be done carefully as the calcium and magnesium that are released in the regeneration can form scaling with anions like carbonate, bicarbonate and sulphate. The water savings were minimal (0.5 BV) and similarly the chemical use reduction can also be expected to be less than 1.5 %. Nevertheless, this may be interesting in newly built plants since the additional piping and automation is minimal.

7. Acknowledgments

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List of abbreviations

BGAC	Biological granular activated carbon
CapEx	Capital Expenditure
CCRO	Closed-circuit reverse osmosis
CIP	Cleaning in place
COD	Chemical oxygen demand
DO	Dissolved oxygen
EDR	Electrodialysis reversal
EDI	Electrodeionization
GAC	Granular activated carbon
IC	Inorganic carbon, ion chromatography
IEX	Ion exchange
IMPROVED	Integrale Mobiele PROceswater Voorziening voor een Economische Delta
MABR	Membrane aerated bioreactor
MB	Mixed bed resin
MTC	Mass transfer coefficient
NDP	Net Driving Pressure
NPD	Normalized Pressure Drop
NSP	Normalized salt passage
OpEx	Operational Expenditure
PFRO	Pulse-flow reverse osmosis
RO	Reverse osmosis
SAC	Strong Acid Cation
TC	Total Carbon
TOC	Total organic carbon

Appendices

Appendix 1

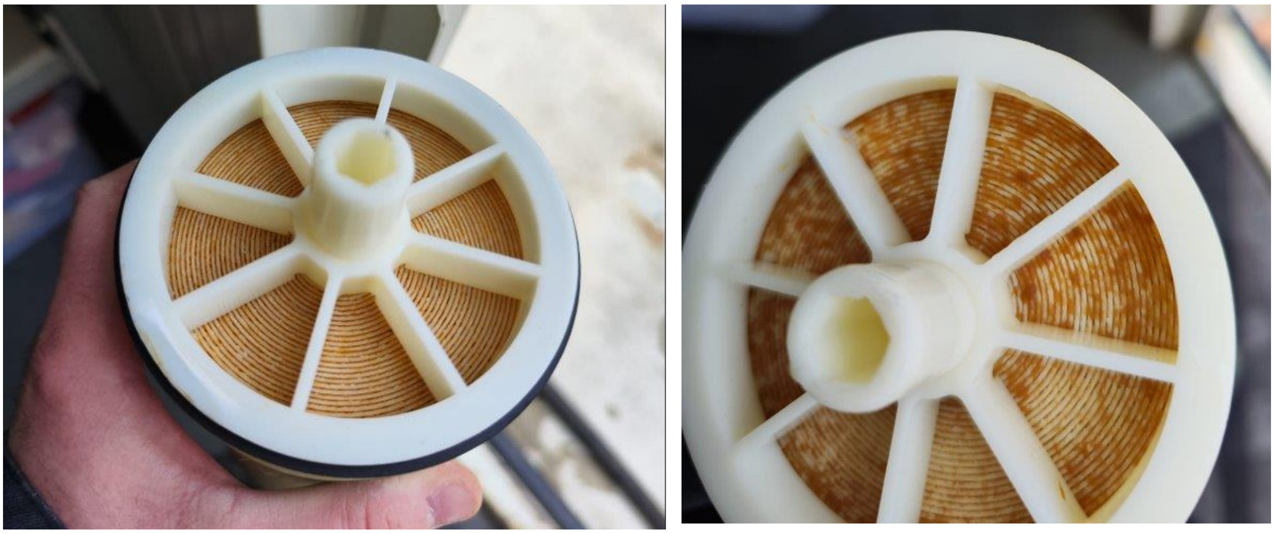

Figure 26 RO membrane feed side (left) and concentrate side (right)

Figure 27 Opened RO membrane

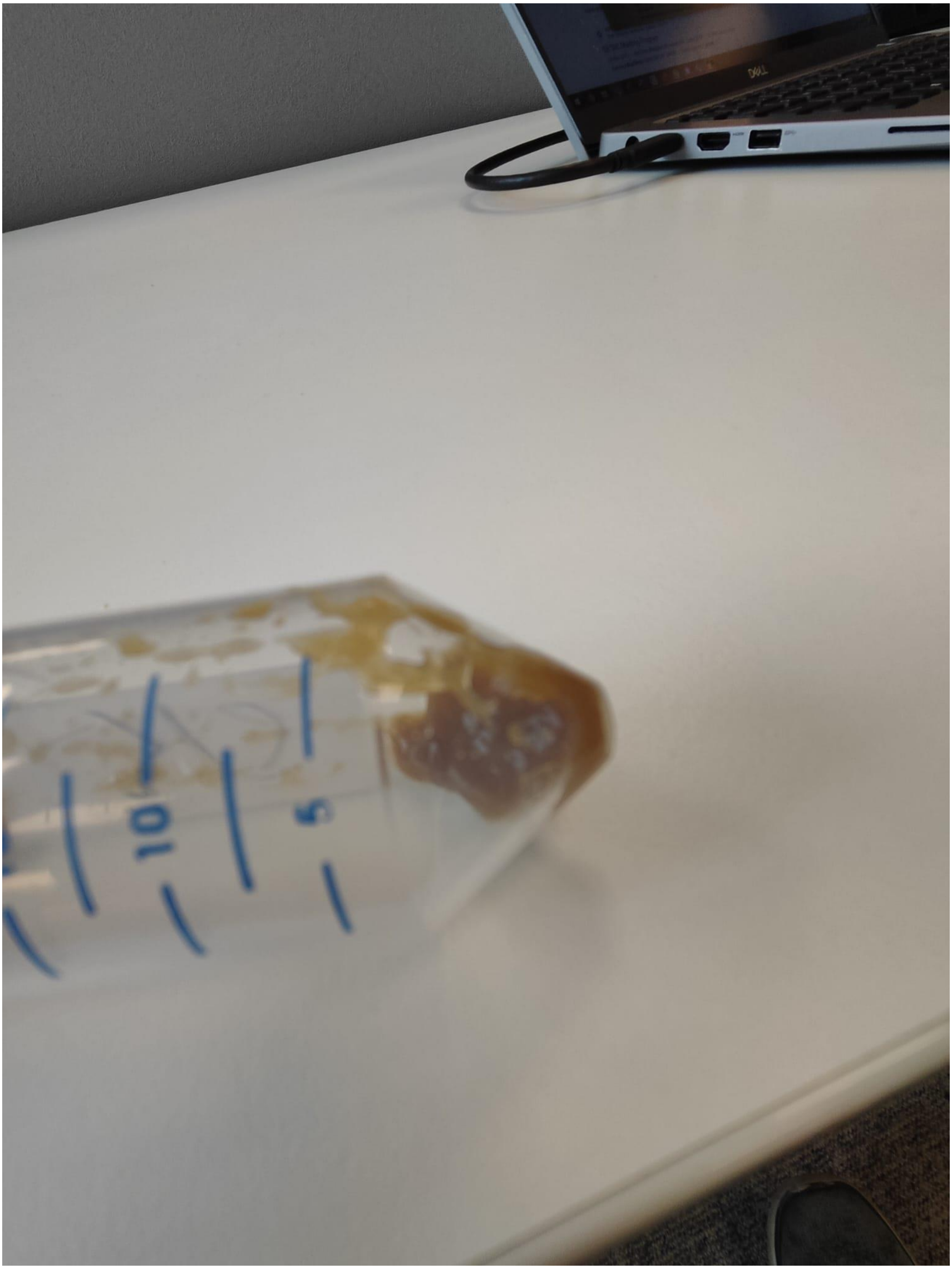

Figure 28 Fouling sample collected for analysis

Appendix 2. Equations used in the RO normalization

$$SP = EC_p \times T_{cf\_EC} \times Q_{cf}$$

$$EC_p = 100 \times \frac{EC_{permeate}}{(EC_{feed} \times \left(log \frac{1}{1 - Recovery}\right))/Recovery}$$

$$T_{cf} = exp^{(U_{par} \times \left(\left(\frac{1}{T_{feed}+273.15}\right) - \left(\frac{1}{T_{ref}+273.15}\right)\right))}$$

Where U_{par} is the DuPont membrane U-value, equal to 3200, EC_p is the recovery corrected permeate conductivity, T_{ref} is the reference temperature equal to 25 °C and T_{cf} is the conductivity corrected temperature.

$$NPD = dP \times Q_{cf} \times T_{cf}$$

$$dP = P_{feed} - P_{concentrate}$$

$$Q_{cf} = \left(\frac{Q_{vc}}{\frac{Q_{permeate} + Q_{concentrate}}{2}}\right)^m$$

$$Q_{vc} = \frac{Q_{feedn} + Q_{concentraten}}{2}$$

$$T_{cf} = \left(\frac{\eta_{ref}}{\eta_{feed}}\right)^n$$

Where NPD is normalized pressure drop [kPa], Q_{feedn} normalized design feed flow of the RO system [$m^3.h^{-1}$], $Q_{concentraten}$ normalized design concentrate flow [$m^3.h^{-1}$], T_{cf} is the viscosity corrected temperature, Q_{vc} is the viscosity corrected flow, η_{ref} and η_{feed} are reference and feed viscosity respectively, m and n are DuPont membrane values, equal to 1.6 and 0.4, respectively.

$$MTC = \frac{Q_{permeate} \times T_{cf} \times 10^{-5}}{36 \times Q_{pemeate}}$$

$$NDP = \left(\left(\frac{P_{feed} + P_{concentrate}}{2} - P_{permeate}\right) \times 100\right) - \left(\frac{OP_{feed} + OP_{concentrate}}{2} - OP_{permeate}\right)$$

$$T_{cf\_OP} = \frac{T_{feed} + 273.15}{T_{ref} + 273.15}$$

$$OP_{feed} = EC_{feed} \times EC_{OP\_feed} \times T_{cf\_OP}$$

$$OP_{concentrate} = EC_{concentrate} \times EC_{OP\_concentrate} \times T_{cf\_OP}$$

$$OP_{permeate} = EC_{permeate} \times EC_{permeate} \times T_{cf\_OP}$$

Where MTC is the mass transfer coefficient [m.S^{-1}.Pa^{-1}], NDP net driving pressure [kPa], OP osmotic pressure calculated for feed, permeate and concentrate [kPa] and T_{cf_OP} is the osmotic pressure corrected temperature.