

Report IMPROVED

Mobile Research Infrastructure Experiments

Case study at BASF Antwerp N.V.





The Improved containers on site at BASF Antwerp, photography by Michel Wiegandt, BASF

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Contents

1.	Introduction.....	6
a)	Problem Statement	6
b)	Goal.....	7
2.	Technologies of interest	7
a)	Ion exchange.....	7
b)	Reverse osmosis	8
c)	Membrane distillation and stripping	9
d)	Electrodialysis	11
3.	Materials and Method.....	12
a)	Ion exchange.....	12
b)	Reverse osmosis	12
c)	Membrane distillation and membrane stripping	12
d)	Electrodialysis	13
e)	Economic evaluation	13
4.	Results and Discussion.....	13
a)	The Biesbosch case	13
	Ion exchange.....	13
	Reverse osmosis.....	15
	Membrane distillation	20
	Electrodialysis reversal	22
b)	F200 process condensate case	24
	Reverse osmosis.....	25
	Membrane Stripping.....	31
c)	General condensate stream	33
	Reverse osmosis.....	35
	Mixed bed	38
	SAC followed by mixed bed	40
	Electrodialysis reversal	41
d)	Economic analysis	43
	The Biesbosch case	43
	The F200 case	45
	The general condensate stream	46
5.	Conclusion	48
	The Biesbosch case.....	48

F200 process condensate.....	48
General condensate stream.....	49
6. Acknowledgments	49
7. References	50
List of abbreviations	51
Appendices	52
A.1 Composition of the Biesbosch period RO feed water and RO permeate	52
A.2 Composition of the F200 for the November period.	54
A.3 Economic analysis	55
The Biesbosch case	55
The F200 case	58
The general condensate stream (GDW)	60
A.4 Used equations.....	63

1. Introduction

Fresh water is of major importance for the chemical industry, as it is used in all kind of chemical processes. However, the continuous supply becomes more uncertain nowadays, as ground and surface water are depleting. 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 technologies for demineralized water production from surface water and spent condensates is investigated for the case of BASF Antwerp N.V., in the context of the IMPROVED project (Integrale Mobiele PROceswater Voorziening voor een Economische Delta).

a) Problem Statement

In 2011, BASF Antwerp N.V., largest producer of raw chemicals, changed from drinking water to Biesbosch surface water, both water sources that need demineralization before use in steam-water cycles for energy production. The ion exchange (IEX) demineralization unit that was already present was optimized for use on tap water and did not change with the altered water source. Before transport to BASF Antwerp N.V., the Biesbosch surface water is treated by multi-media filtration and monochloramine (MCA) is added by Evides Industriewater as an antimicrobial agent as well as FeCl_3 as a coagulant. The question is whether IEX is still the most efficient and ecological treatment for the altered water source. The high feed water conductivity (450 - 600 $\mu\text{S}/\text{cm}$) and the seasonal variation in Total Organic Carbon (TOC) concentration (range of 2 - 3 mg/l) require a robust and reliable treatment technology. Reverse osmosis (RO), which is a state-of-the-art desalination technology, might be a better alternative considering both chemical consumption and end water quality. Membrane distillation (MD) and Electrodialysis Reversal (EDR) were also tested on the surface water to investigate the TOC removal as well as deionization.

In addition to the Biesbosch surface water, two process condensate streams were investigated. The GDW condensate is the combination of all condensates inside the plant. Overall, the quality of this stream is close to boiler feed water even before treatment. The main constituent is ammonia, which is added as an alkalinizing agent in order to increase the pH, which mitigates corrosion. The currently used technology is a mixed bed (MB), which is exhausted mainly due to the presence of the ammonia. The second condensate stream of interest was the F200 stream, which contains a lot of alcohols (t-butanol, isopropanol and methanol) as well as acetone. As these components are uncharged, they cannot be removed by the conventional IEX processes. Since the F200 stream is one of the larger condensate streams and has a typical TOC values of 450 - 700 $\mu\text{g}/\text{l}$. In general, TOC is problematic in steam-water cycles as it might break down to organic acids under high temperatures and pressures, which can induce corrosion to the equipment. Therefore, currently the F200 stream is not reused as boiler feed water, but as process water instead.

b) Goal

For the Biesbosch surface water, IEX was investigated as the reference technology. Not only the water quality was tested but also the behavior of both TOC and microbiology throughout the IEX set-up was determined by performing total organic carbon (TOC), liquid chromatography organic carbon detection (LC-OCD) and flow cytometry (FCM) analyses. Reverse osmosis (RO) was tested and might be a better alternative considering both chemical consumption and end water quality. Membrane distillation (MD) was also tested on the surface water to investigate the overall TOC and conductivity reduction.

In order to remove the ammonia prior to the mixed bed (MB) treatment in the GDW condensate (also called general condensate stream in this report), different technologies were investigated. While MB was the reference, RO and electrodialysis reversal (EDR) were studied as possible stand-alone desalination technologies. Another option, with most probably less initial investment costs, was to first remove the ammonia by adding a strong acid cation (SAC) ion exchange column in front of the MB. The alcohols in the F200 stream were treated with RO and membrane stripping (MS).

2. Technologies of interest

a) Ion exchange

IEX is an electrochemically driven process. Ions are removed from the solution, because they are exchanged with ions already present on the IEX resin. In this specific case, regenerated cation resin (weak acid cation (WAC) and strong acid cation (SAC)) has H^+ , while regenerated anion resin has OH^- (strong base anion (SBA)) or a free base (weak base anion (WBA)) connected to its functional groups. The degasser (DG) removes CO_2 after cations are removed, therefore lowering the bicarbonate load to the anion resin. The mixed bed (MB) contains both SAC and SBA resin and polishes the water to $< 1 \mu S/cm$ electrical conductivity (EC). The mixed beds can also be operated separately as a condensate polishing unit (CPU). As the IEX module removes ions, the resin slowly gets saturated, creating the need for a regeneration. By measuring pressure, EC, pH, TOC, sodium (Na) and silica (Si) before and after selected columns, the quality of the process can be monitored. A general overview of the IEX layout is provided in Figure 1. For more details about the operation of the IEX module, consult the document 'Functional Description IEX-MB'.

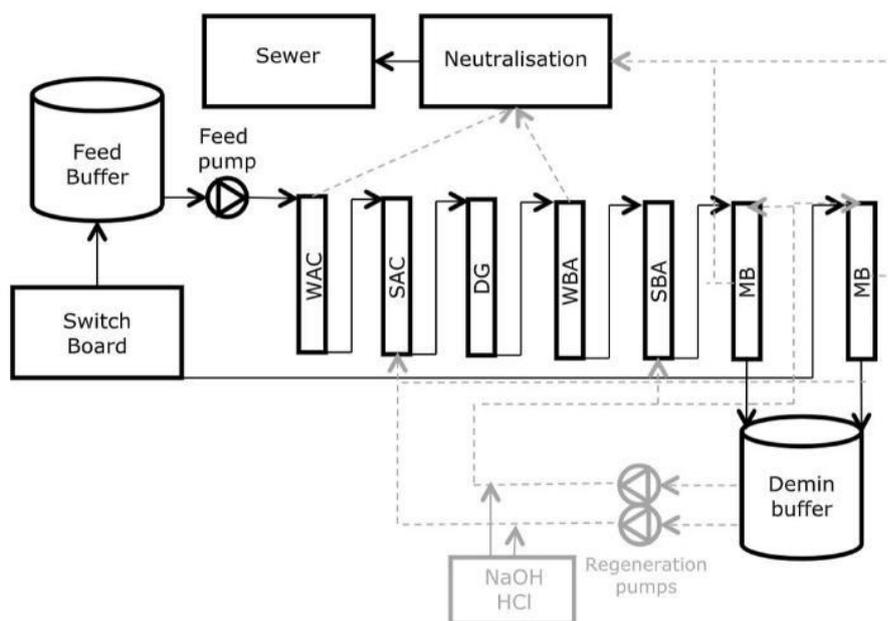


Figure 1. Schematic overview of the IEX module.

b) Reverse osmosis

In RO, a pressure gradient leads to separation through a semipermeable membrane. Salts, suspended solids, viruses, and dissolved components are retained in the concentrate, while water and some limited dissolved components move through the membrane in the permeate. RO membranes are typically not cleaned by backwashing, but are mostly cleaned-in-place (CIP), or can be flushed with air (AIRO) to remove fouling and prevent clogging of the feed spacer. A general overview of the RO layout is provided in the Figure 2. For more details about the operation of the RO module, consult the document ‘Functional Description RO’.

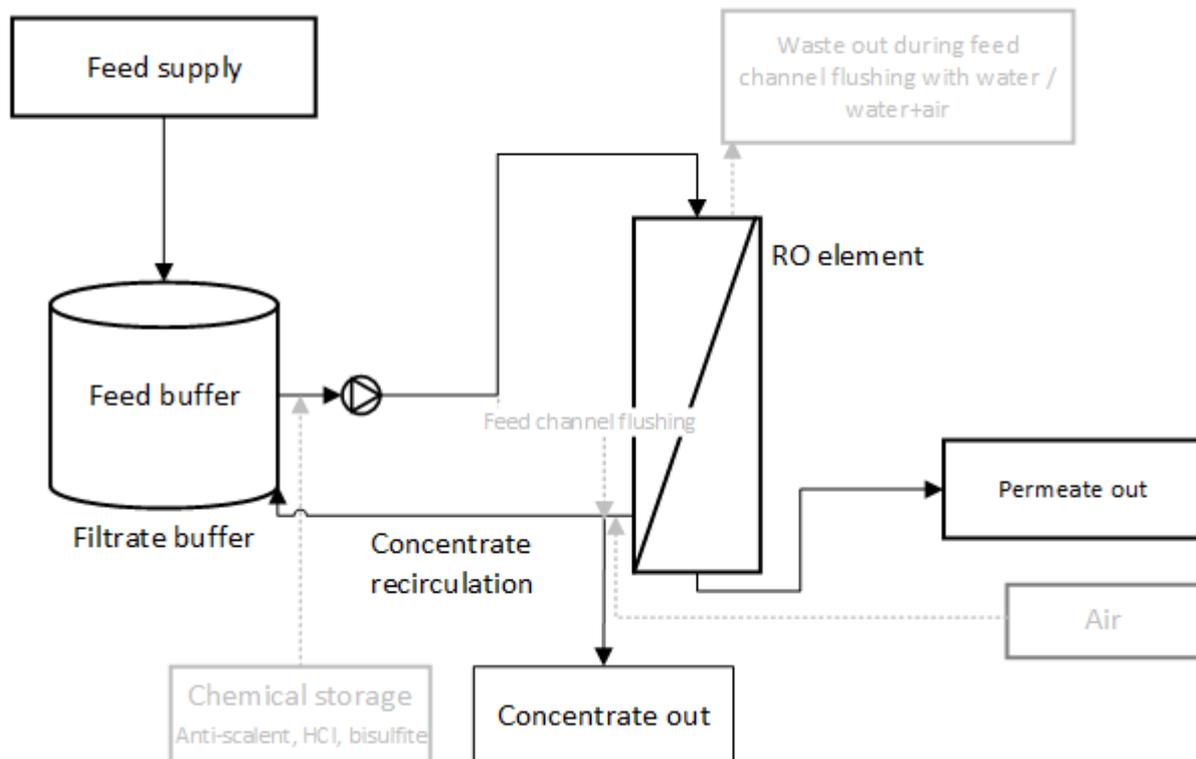


Figure 2. Schematic overview of the RO module.

c) Membrane distillation and stripping

Membrane distillation is an example of thermally-driven membrane processes. The hydrophobic membrane only allows passage of volatile (water vapor, ammonia and others), while retaining all non-volatile components, amongst which salts and trace organics.

The MD unit may be run in various modes, being:

- Membrane stripping: removal of dissolved gasses/volatile components in the feed by providing a driving force in terms of vapor pressure difference. In membrane stripping, this often is done by providing a pH difference across the membrane.
- Direct Contact MD: whereby the porous hydrophobic membrane acts as the only barrier between feed and receiving phase and a temperature gradient is used as the driving force;
- Air-Gap MD: whereby an additional air gap and cooling wall are installed between the membrane and the cooling phase, but temperature is also the driving force. This air gap reduces the conductive losses through the membrane by acting as the limiting thermal resistance.

For the case study BASF, the MD module was used in the MS mode and in DCMD mode. A general overview of the MD layout is provided in Figure 3. For more details about the operation of the MD module, consult the document 'Functional Description MD'.

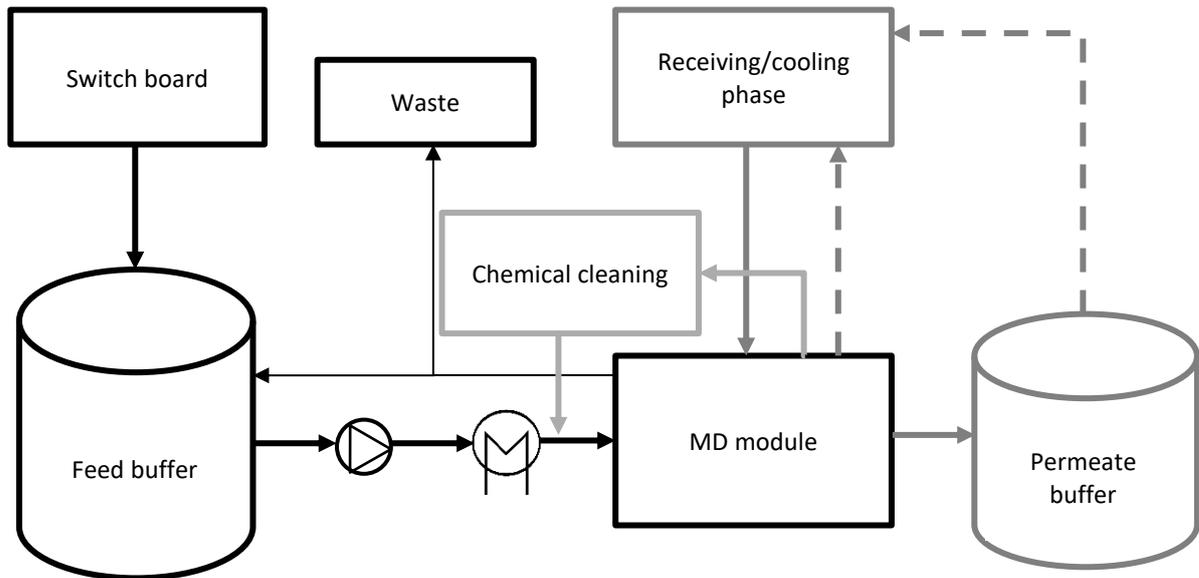


Figure 3. Lay-out of the MD skid

A more in-depth view on the working mechanism of both MD and MS is shown in Figure 4. Here, the difference in temperature or pH is of most importance, respectively.

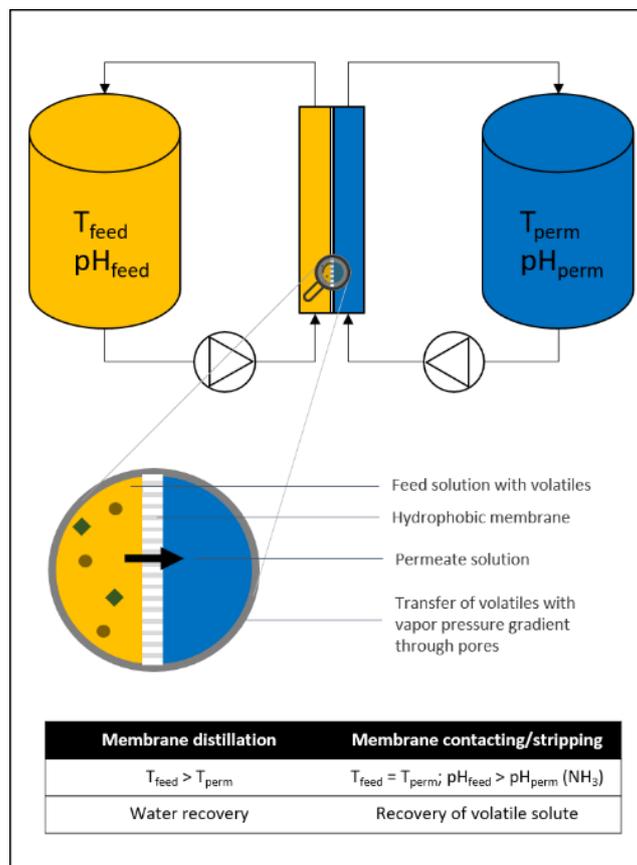


Figure 4. Schematic representation of membrane distillation and stripping, the driving force is provided by a difference in temperature or pH, respectively [1].

d) Electrodialysis

Electrodialysis is a desalination technique in which separation of ions and water is achieved by applying an external potential across semipermeable membranes. Here, Anion Exchange Membranes (AEM) and Cation Exchange Membranes (CEM) are altered in the ED unit in order to establish desalination of the diluate stream and to transport the ions to the concentrate. A general overview of the ED layout is provided in Figure 5. For more details about the operation of the ED module, consult the project document ‘Functional Description ED’.

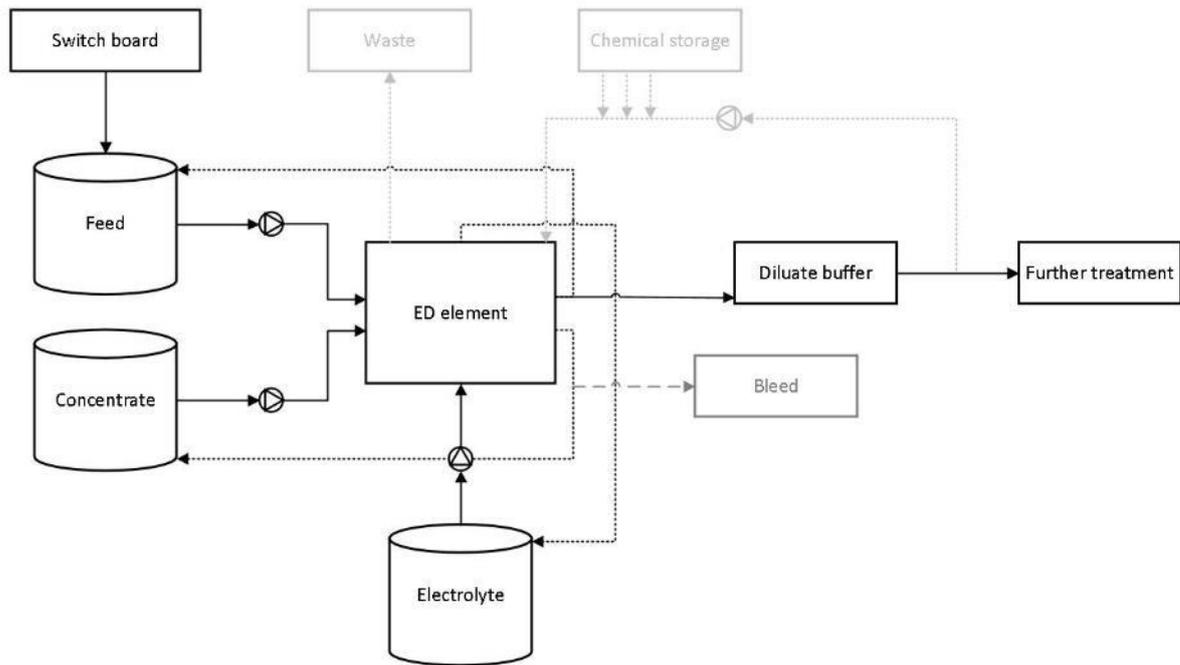


Figure 5. Schematic overview of the ED module.

A more in-depth view on the working mechanism of the ED module, with the respective cell pair configuration, is shown in Figure 6. The ED 1000A module from PCCell consisted of 25 cell pairs.

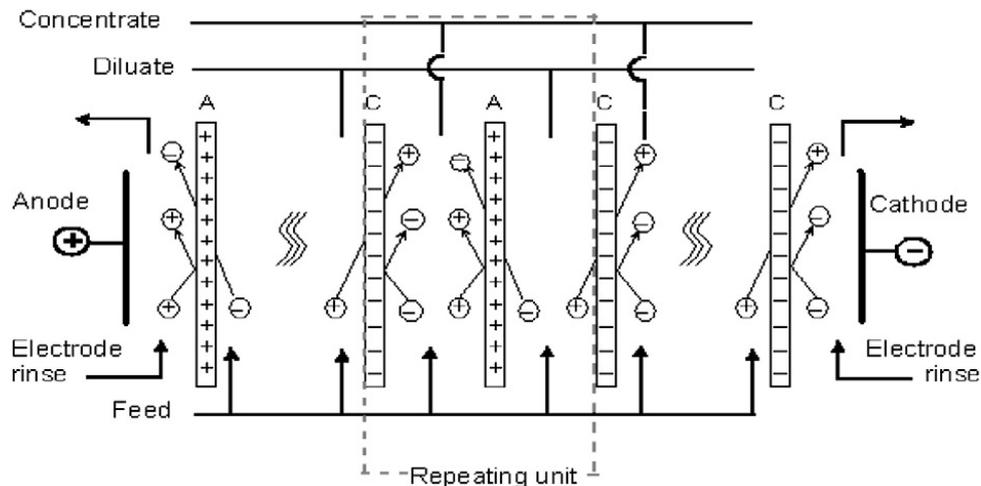


Figure 6. Separation mechanism in an ED module [2].

The electrode rinse in Figure 6 is the electrolyte, which was a solution of 1M NaNO₃ (55 mS/cm) for the Biesbosch water and was diluted to 5 mS/cm on Oct 16 2018.

3. Materials and Method

a) Ion exchange

The resins used in this setup are supplied by Dow - **Table 1**:

Table 1. Arrangement and resin type inside the IEX setup

Column	Bed height, fresh (cm)	Resin	Column height (cm)
WAC	79 (6.2L)	Marathon 8300	85
SAC	136 (10.6 L)	Marathon 1200 H	145
Degasser			
WBA	116 (9.1 L)	Marathon 9600	145
SBA	136(10.6 L)	Amberjet 9000 OH	145
MB1	140 (10.9 L)	Marathon 1200 H* (40%) + Ambertjet 9000 OH (60%)	145
MB2	139 (10.9 L)	Marathon 1200 H* (40%) + Ambertjet 9000 OH (60%)	145

* Replaced with Dowex 650C (H) on 7 Sep 2018

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

b) Reverse osmosis

In Figure 2, the scheme of the RO set-up is shown. The RO membrane was a Dow Filmtec LC HR-4040, with an active membrane area of 8.7 m². The pressure housing was a Codeline 40E100 (Lenntech, The Netherlands). The pH, flow, pressure, conductivity, free chlorine and temperature were continuously measured online with 2-minute sampling intervals. Nalco Permtrat 191T was used when antiscalant dosing was required.

c) Membrane distillation and membrane stripping

In Figure 3 the scheme of the MD set-up is shown. The MD membrane was a polyethylene membrane in a spiral wound module (Aquistill, the Netherlands). The active membrane area was 7.2 m². Further details on the module cannot be given due to confidentiality. The feed and permeate flow were set to 650 l/h.

The feed temperature was kept at a setpoint of 50 °C and the permeate temperature at a setpoint of 30 °C. While other temperature setpoints were also attempted, one of the two heating elements failed and the majority of the experiments were conducted at the maximal power that the system could achieve with the remaining single 9 kW heater.

d) Electrodialysis

In Figure 5 the scheme of the ED set-up is shown. The ED stack is an ED 1000A (PCCell, Germany). The membranes used were PC SK (CEM) and PC AV (AEM). The power source was a SM 60-100 (Delta Elektronika, The Netherlands). The pH, flow, pressure, conductivity, voltage and current were continuously measured online.

e) Economic evaluation

An economic analysis was performed for the different water technologies for all water streams (Biesbosch surface water, the GDW condensate and the F200 stream) by Evides Industriewater. This was done in order to evaluate the economic viability of the treatment technologies for each stream and to discuss the trade-off between the obtained product water quality and the investment costs.

4. Results and Discussion

In this chapter, the results of all the demineralization technologies on the three different water streams is discussed. First the Biesbosch experiments are provided, then the GDW stream experiments, followed by the F200 case.

a) The Biesbosch case

The Biesbosch case water is mixture of mainly Biesbosch water mixed with some potable water, typically between 10-20 percent, but this percentage can vary from day to day. Before arriving at the BASF site, monochloramine (MCA) is added by Evides Industriewater as a biocide in order to suppress biological activity, resulting in average concentrations of 11 $\mu\text{g/l}$ free chlorine and 1.74 mg/l bound chlorine on average, measured by BASF. However, the MCA in high concentrations can damage ion exchange resins, therefore, before treatment, sodium bisulfite (SBS) is added to neutralize the MCA. The Biesbosch water with MCA and SBS is also preheated in BASF to around 30 degrees to enhance the ion exchange kinetics. The testing was done on Biesbosch water with MCA and SBS and preheating as well as Biesbosch with MCA without SBS. For a short period of time Biesbosch with MCA with 80 to 90 percent of potable water added was also tested at the containers.

Ion exchange

The Biesbosch surface water was treated with IEX after MCA dosing during a two-week period (25-10-2018 until 8-11-2018). During this period of time, the TOC concentration of the incoming water was elevated due to seasonal variation. Concentrations higher than 4 mg/l TOC were measured in the days before the treatment began. However, the average TOC value during the experiments was only 2.3 mg/l and the average conductivity was 596 $\mu\text{S/cm}$. The overall composition of the feed water is given in Table 2.

Table 2. Composition of the process water with Biesbosch as feed water.

	pH	Temp.	Cond.	NH ₃	SiO ₂	PO ₄	Cl	SO ₄	NO ₂	N	Br
	-	°C	µS/cm	mg/l	mg/l	µg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Average	8.36	7.03	596.00	0.21	4.23	20.78	69.33	58.31	0.17	9.73	0.16
σ	0.11	1.69	28.05	0.07	0.28	6.92	20.42	4.30	0.06	6.83	0.03
	F	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC
	mg/l	mg/l	µg/l	µg/l	µg/l	mg/l	mg/l	mg/l	µg/l	µg/l	mg/l
Average	0.32	59.13	1.60	1.10	24.43	6.52	7.80	45.59	2.12	8.06	2.31
σ	0.06	9.28	0.00	0.12	5.50	0.66	0.76	5.54	0.45	0.74	0.48

As can be seen in Figure 7, the incoming feed water quality varies largely between days based on the conductivity, but even within hours the water conductivity fluctuates.

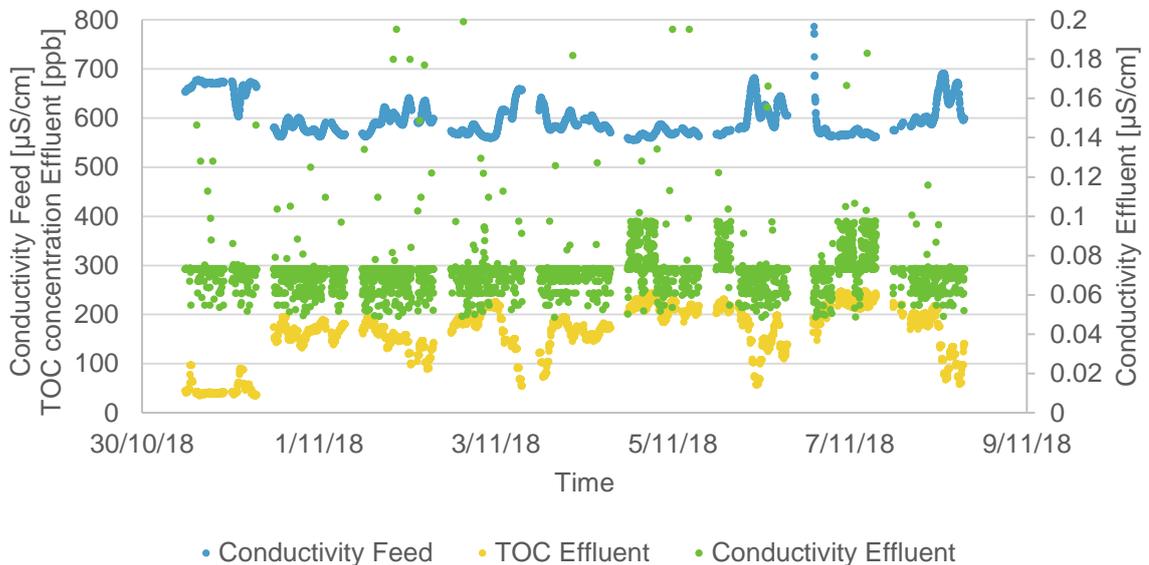


Figure 7. The general course of the Biesbosch feed and effluent degassed cation conductivity during IEX treatment.

The effluent degassed cation conductivity was always below the threshold value of 0.2 µS/cm. This results in a removal efficiency of 99.99% based on conductivity alone. Despite the fact that the incoming feed water quality varies a lot over days, and even hours, the end water quality is more or less stable. The TOC concentration was always below the desired 250 µg/l threshold value, the TOC removal efficiency was 94% on average. An interesting observation is the fact that the effluent TOC concentration has an inverse relationship with the conductivity of the feed water. More research is needed to explain this phenomenon. The TOC concentration in the effluent of each column is given in the table below.

Table 3. The TOC concentration of the effluent of the respective IEX column. Values are given in µg/l.

Time	Feed	WAC	SAC	Degasser	WBA	SBA	MB
31-10-'18	1600	1400	1430	1500	-	60.7	37
2-11-'18	2130	1480	2020	2090	-	153	80
5-11-'18	3000	1850	-	2430	291	230	229
6-11-'18	3000	1950	-	1640	1080	164	129
7-11-'18	2380	2200	1580	2200	260	233	207
8-11-'18	2350	2090	1920	2130	-	167	222

As shown in the masterthesis conducted prior to the pilot scale experiments, the scavenger is able to remove more than 50% of the TOC in the feed water [3]. This way, the subsequent WBA and SBA are even more protected against a TOC overload and/or (ir)reversible fouling of the resins.

The calculation of the water efficiency was based on a downtime of 1 hour at a regeneration flow equal to the production flow (250 l/h). These parameters are an overestimation, resulting in a water efficiency of 96%.

After the MB, the effluent was analyzed and the results are given in the table below. Mark the difference in units for Cl, Ca, K, Mg and Na.

Table 4. Composition of the effluent after IEX followed by mixed bed treatment on the Biesbosch water.

	pH	Temp	Cond.	NH ₃	SiO ₂	PO ₄	Cl	SO ₄	NO ₂	N	Br
	-	°C	µS/cm	mg/l	µg/l	µg/l	µg/l	mg/l	mg/l	mg/l	mg/l
Average	-	-	0.07	<0.05	0.76	<10	<100	<0.10	<0.10	<0.10	<0.10
σ	-	-	0.01	-	-	-	-	-	-	-	-
Removal (%)			99.99	-	82.03	-	-	-	-	-	-
	F	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC
	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	mg/l
Average	<0.10	<10	<0.8	<1	3.88	23.50	6.14	58.43	<1	<1	133.09
σ	-	-	-	-	2.27	12.09	3.27	32.44	-	-	82.21
Removal (%)	-	-	-	-	84.12	99.64	21.28	98.72	-	-	94.24

The IEX treatment is capable to remove most of the ions below the limit of detection. The few ions which are left in the effluent are situated in the µg/l range. The produced end water quality is more than acceptable for use as boiler feed water.

Reverse osmosis

The RO treatment was applied to the Biesbosch water in a total of 4 periods, but the most representative experiments are from 3rd to 20th of July when it was applied to pre-heated Biesbosch water neutralized with sodium bisulfite and from Oct 17th to Nov 8th where it was applied to Biesbosch water without sodium bisulfite (SBS) neutralization. For a very short period between 20th and 23rd of July RO was applied to a stream consisting of mainly potable water (80-90%), mixed with Biesbosch water with MCA without SBS.

The neutralized and pre-heated stream had an average temperature of 27.4 °C, while the MCA-only stream had a temperature of 16.8 °C. The composition of the Biesbosch feed water for the period of running on Biesbosch with MCA and sodium bisulfite can be seen in Table 5.

Table 5. Laboratory analysis of the Biesbosch water with MCA and SBS neutralization 3/07/2018 to 20/07/2018.

	pH	Temp.	Cond.	NPOC	NH ₃	SiO ₂	PO ₄	Cl	SO ₄	NO ₂	NO ₃	Br
		°C	µS/cm	mg/l	mg/l	µg/l	µg/l	µg/l	mg/l	mg/l	mg/l	mg/l
Average	7.8	27.4	470	2.1	0.2	3417.1	10.2	49796	43.4	0.3	11.3	0.3
σ	0.2	2.8	5	0.1	0.1	257.3	1.1	2423	3.3	0.2	1.2	1.4
	F	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC	
	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	
Average	0.2	51727	0.8	1.1	29.94	5642	6718	32519	2.3	7.5	2425	
σ	0.0	7753	0.0	0.2	16.28	1141	1013	6230	0.4	2.5	63	

While the Biesbosch water is continuously mixed with 10-20 % potable water, during the period of 24 to 27th of July, the water was composed mainly of potable water (54 percent potable) - Appendices Table 26. The composition of the Biesbosch and the Biesbosch mixed with 54 % of potable is relatively similar in terms of ions and conductivity, but the TOC and non-purgeable organic carbon (NPOC) of the potable water is much lower.

During the third period where the RO was applied on Biesbosch with MCA without SBS - Appendi Table 28. During this period the ion content was elevated as well as the conductivity with average value of 566 µS/cm. The TOC was similar as an average value to the with SBS neutralization but had larger variation with values as high as 3000 and as low as 1600 µg/l, suggesting that it was also mixed with some amount of potable water during the low TOC measurements, since the TOC in the fall is usually the highest due to decomposition of leaves and organic matter.

In the beginning of the experiments, the RO was running without antiscalants, but this quickly led to rapid escalation of pressure, which was semi-reversibly cleaned with acidic cleaning in place. Previous attempts to clean it with base failed, confirming that the problem was indeed scaling and not biofouling. Further testing of samples from the membrane autopsy using flow cytometry also ruled out biofouling. When the system was adapted to run with antiscalants, there were no obvious signs of scaling on the membrane.

The RO permeate quality was stable without the SBS neutralization and the membrane did not show any signs of decreasing rejection due to oxidation of the active layer during the one week run between 20th and 27th of July as well as during the 3 weeks of testing in the period October-November confirmed the stability of rejection, which suggests that if needed, the RO can be ran with the MCA-only stream that can prevent possible biofouling on the membrane. The specification sheet of the membrane specifies the upper limit of free chlorine to be 100 µg/l, while the average free chlorine measured by BASF was 11 µg/l, which suggests the possibility to operate the RO without free chlorine neutralization by SBS. Prolonged exposure of the membranes to free chlorine can shorten the membrane lifetime due to oxidation, but fouling which can be prevented by the MCA, can also shorten the lifespan of the membranes.

While the membrane module itself did not show any signs of biofouling while running on Biesbosch water, clear signs of biofouling were seen on the cartridge filters (60 µm) that pretreated the incoming water. The biofouling on the cartridge filters was observed only when the RO was running with antiscalants (3.3 mg/l Nalco Permatreat 191T). The biofouling on the cartridge filters was not observed while running on water with MCA and without sodium bisulfite neutralization. The antiscalant is easily biodegradable which explains the biofouling due to the added nutrients in the water during the recirculation.

It is worth noticing that contrary to a typical full-scale RO system, the RO in the IMPROVED containers recirculates some of the concentrate to the buffer tank in order to achieve high recovery and still have adequate flow velocity inside the feed spacer channel of the RO. Another option is to only simulate the first element in a RO without using recirculation, but the choice was made to have recirculation and to simulate the complete train.

Operating the RO with recirculation comes with two drawbacks. In a full-scale system, several modules are placed in series, and the first modules are operated at high flux while the concentrations are still low, while the last modules are operated at lower flux to prevent scaling at the higher concentrations. In the containers, a single module needs to achieve the final rejection while having a quite high average flux, which can aggravate the problem of scaling. Moreover, typically the antiscalants work by slowing down the crystal growth and breaking down the crystals by corrupting their structure. At full-scale, the water is passed only once through the series of modules and discharged, while at IMPROVED, the feed as well as the contained crystals are recycled, which can also aggravate the scaling problem because the crystals can continue to grow despite the added antiscalants. Perhaps Genesys RC can be used in future tests as this antiscalant is known to be better suited for systems with recirculation.

The composition of the RO permeate for the period of 20-27 July can be seen in Table 6.

Table 6. Composition of the RO permeate running on Biesbosch water with MCA and SBS neutralization 3/07/2018 to 20/07/2018.

	Cond.	NH ₃	SiO ₂	PO ₄	Cl	SO ₄	NO ₂	NO ₃	Br	F
	μS/cm	mg/l	μg/l	μg/l	μg/l	mg/l	mg/l	mg/l	mg/l	mg/l
σ	1.0	0.0	11.3	1.1	143.4	0.0	0.0	0.2	0.0	0.0
Aver.	12.8	<0.1	71.9	10.3	1133	<0.1	<0.1	1.3	<0.1	<0.1
Rejection (%)	97.3		97.9	-1.0	97.7			88.5		

	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC
	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l
Aver.	142.2	<0.8	<1.0	1.4	346.3	33.7	1859	<1.0	<1.0	N/A
σ	134.5	0.0	0.0	1.4	38.8	24.2	178.5	0.0	0.0	N/A
Rejection (%)	99.7			95.3		99.5	94.3		86.7	N/A

As seen in Table 6 the RO has excellent rejection for most components, but still needs further treatment if the aim is to use it as boiler feed water. This is mainly due to the remaining salts in the system. To meet boiler feed water standards, a degassed conductivity of less than 0.2 μS/cm is needed. The permeate still has a specific (raw) conductivity of 8.2 μS/cm. A mixed bed or polishing with electro deionization (EDI) will likely bring the water to specifications for boiler feed water.

While the TOC was measured during this period, the instruments were operated without inorganic carbon (IC) removal, which is needed for ratios of IC/TOC higher than 10. Therefore, the measured values for this period are likely invalid. For the run of the RO in the same conditions for the three weeks in October-November the measured TOC was 45.7 (± 40.8 μg/l) or a rejection of 98.1%, which is much lower than the imposed 250 μg/l limit for boiler feed water.

It is interesting to notice that during the period of October-November, due to seasonal variations, the composition of TOC includes a lot of uncharged organics, which lead to 200-250 μg/l of TOC for the ion

exchange skid inside the container and similar behavior was seen in the full-scale installation in the demineralized water facility of BASF. Therefore, the RO showed a significant advantage in the rejection of TOC, even after a single pass.

The rejection for the run on the MCA-only stream was better for all components that could be measured with confidence (i.e. above their detection limit), which can be explained by the lower feed temperatures, since generally RO has an inverse relation between rejection and temperature due to increasing ion mobility inside the membrane matrix at elevated temperatures. As an overall indicator, the conductivity of the permeate on MCA-only stream was 8.2 $\mu\text{S}/\text{cm}$, compared to 12.2 $\mu\text{S}/\text{cm}$ for the warmer Biesbosch stream with bisulfite neutralization.

To better analyze the performance of the RO, the membrane mass transfer coefficient, normalized salt passage and the normalized feed channel pressure drop was analyzed according to the guideline published by Kiwa [4] (Appendix A.4 Used equations).

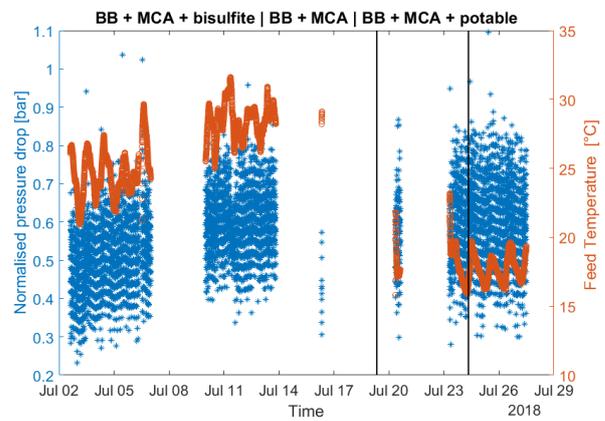
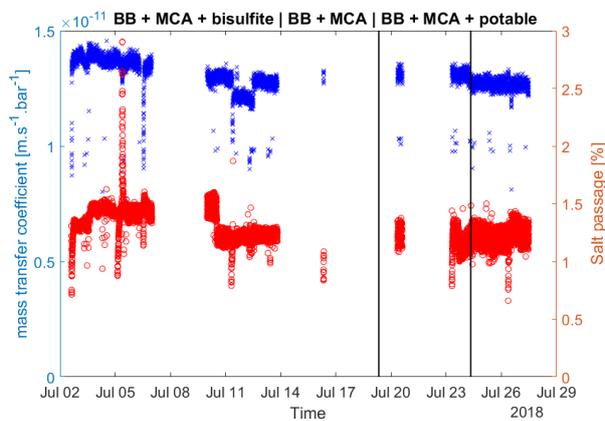


Figure 8. Membrane mass transfer coefficient and normalized salt passage for the period of July

Figure 9. Normalized feed channel pressure drop and feed temperature for the July period

The experiments for this period were started with a virgin membrane, therefore the loss of c.a. 15% membrane mass transfer coefficient in the first week is rather normal (**Figure 8**). For the following experiments it remained rather constant. Similarly, there was no problem with increase of normalized salt passage even for the period operated on MCA without SBS neutralization. The normalized feed channel pressure drop (seen in **Figure 9**) increased rapidly during the first week and then remained at a plateau value of around 0.6 bar, which is also expected.

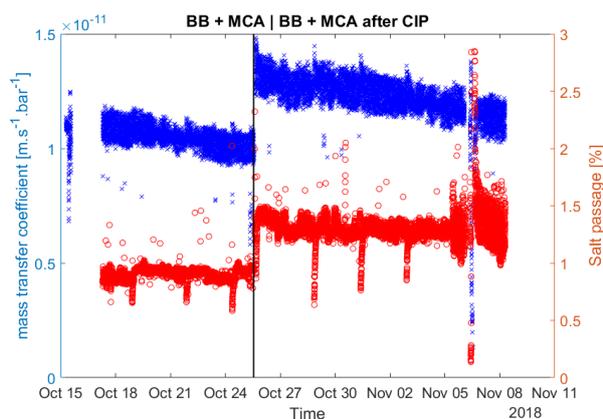


Figure 10. Membrane mass transfer coefficient and normalized salt passage for the period of Oct-Nov

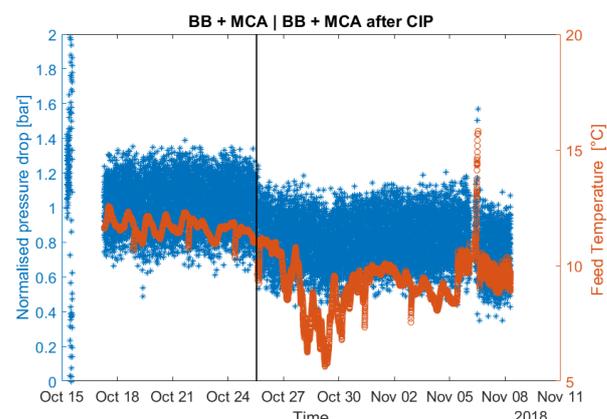


Figure 11. Normalized feed channel pressure drop and feed temperature for the Oct-Nov period

For the period Oct-Nov the system was operated with a pre-fouled membrane from a run on the F200 stream. As discussed in the RO section for the F200 case, feed channel spacer biofouling was observed probably caused by iron reducing and/or iron oxidizing bacteria, therefore the pressure drop of the feed channel in the beginning of the experiments is elevated to about 1 bar (**Figure 11**). There was no trend on further increase on the feed channel pressure drop from Oct 15 to Oct 24. This fouling also slightly affected the membrane mass transfer coefficient, but not to a great extent as seen on **Figure 10**. On Oct 25th a Cleaning In Place (CIP) was performed first with HCl at pH 2 for 20 minutes, followed by a basic cleaning in place at pH 12 with NaOH. The acidic cleaning had immediate change in the pressure drop of the channel, which is expected with biofouling. The basic cleaning in place improved the membrane mass transfer coefficient to values observed with a virgin membrane, but had little effect on the feed channel pressure drop. Upon further evaluation, the basic cleaning in place should have been done for a longer period of 1h, possibly at elevated temperatures.

What is also noticeable is the increase in the normalized salt passage after CIP on October 25th - **Figure 10**. Since the CIP was done at pH of 2 and 12, these values are completely within the specification of the membrane of pH 1 and 13. Therefore, no direct effect from the acid and base should be observed on the membrane integrity. It is possible however that the free chlorine contained in the MCA stream probably switched forms from OCl⁻ found at pH above 7 (the usual Biesbosch pH) to HOCl found between pH 2 and 7. HOCl is 80 to 100 times more reactive than OCl⁻. Possibly the acidic CIP pH went below pH 2, where chlorine gas can be formed. Therefore, an important conclusion is that even though the MCA containing stream can be safely treated with reverse osmosis, in case of acidic CIPs, another water source that does not contain MCA should be used or SBS should be added.

On Biesbosch, the system was operated at 75% recovery and 20 l/(m².h) flux. The average transmembrane pressure was 6.25 bar while running on the colder MCA-only stream and 5.05 bar on the warmer MCA and sodium bisulfite containing stream. Considering the membrane area of 8.7 m², the produced permeate had a flow rate of 174 l/h.

The specific energy consumption per cubic meter of produced permeate, considering the permeate flow as well as the concentrate flow, is 1.42 kWh/m³ for the MCA and bisulfite stream and 1.75 kWh/m³ for the MCA-only stream. Considering a feed channel pressure drop of 0.45 bar at a recirculation flow rate of 850 l/h, the

specific pumping energy for the feed channel is 62 W per cubic meter of produced permeate. The average total theoretical specific energy consumption for both periods is 2.26 kWh/m³.

Membrane distillation

The MD skid ran on Biesbosch water for the period of 24/05 until 28/06. Unfortunately, during the start-up, some of the air circulated inside the system became trapped in the enclosure of the first electrical heater, which overheated it and led to its failure. After the tests were completed, the system was adapted to prevent future failures by mounting the heater vessels horizontally instead of vertically.

The following tests were done using the remaining single 9 kW heater and therefore the achieved average temperature difference between the inlets of the hot and the cold compartments was only 13.8°C at a feed inlet temperature of 43.0°C and permeate inlet temperature of 29.2°C, respectively and 650 l/h recirculation flow rate. This is a quite low thermal load for this module and typically it would be operated at 70°C on the feed side and 20°C on the permeate side at a 1300 l/h recirculation flow rate, producing fluxes in excess of 7 l/(m².h) [5].

The flux was frequently measured by manually collecting the distillate into a graduated cylinder for a set time and was calculated to be 0.82 (±0.2) l/(m².h) or 5.9 l/h distillate flow. The low flux is to be expected, given the low driving force applied to the module with a single heater. The energy required to produce 1 m³ of water is calculated based on the power of the electrical heater and the produced distillate flow to be 1523 kWh/m³. It should be noted that this is the thermal energy required, typically supplied as waste heat. In DCMD, this number will always be higher than 660 kWh/m³ (the energy required to evaporate a cubic meter of water), since additional heat is lost via conduction through the membrane matrix.

To improve the thermal efficiency of DCMD, a recuperating heat exchanger could be installed to partially transfer the heat contained in the outlet of the cold channel to the outlet of the hot channel (the hot channel outlet is typically colder than the cold channel outlet in counter current flow configuration at full-scale) and considerably reduce the thermal power requirements. Moreover, the energy recovered with the recuperated heat exchanger will be sent back into the module, increasing the flux.

The specific energy needed to drive the recirculation pumps to produce one cubic meter of distillate is calculated with an average pressure drop of 0.37 bar on the feed side and 0.11 bar on the permeate side and 650 l/h average flow rate is 1.15 kWh/m³ and 0.34 kWh/m³ (both expressed per cubic meter of produced distillate) for the feed and permeate, respectively. The higher pressure on the feed side was due to clogging of the cartridge filters with scaling from the electric heaters, therefore in real world application, the pressure would be similar to the one on the permeate side and the specific pumping energy would be 0.68 kWh/m³.

The water efficiency (recovery) was calculated to be 23.6 (±5.8) %. This efficiency is extremely low for membrane distillation, since this technology is often aimed at zero liquid discharge cases. The recovery is dictated by the ratio of water transported from the feed to the permeate via flux and the water that is bled out via a progressive valve. Unfortunately, this progressive valve was opened too much, leading to a low value for recovery. Future tests would have to be conducted at a higher recovery by closing down the bleed valve as well as running the system at higher fluxes.

Despite the practical troubles with the operation of the membrane distillation, the permeate quality obtained in the tests can provide an objective representation of the application of the technology. As a reference, the composition of the feed of the containers for the period can be seen in Table 7.

Table 7. Standard deviation (σ) and average composition of the feed to the containers.

	pH	Temp	Cond.	NH ₃	SiO ₂	PO ₄	Cl	SO ₄	NO ₂	NO ₃	Br
				mg/l	µg/l	µg/l	µg/l	mg/l	mg/l	mg/l	mg/l
Average	7.82	27.43	469.75	0.18	3417	10.22	49796	43.35	0.32	11.32	0.30
σ	0.21	2.79	5.09	0.10	257	1.13	2423	3.35	0.19	1.24	1.37
	F	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC
	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
Average	0.19	51727	0.80	1.06	29.94	5642	6718	32519	2.34	7.22	2425
σ	0.01	7753	0.00	0.17	16.28	1141	1013	6230	0.40	1.25	63

Most of the components measured inside the Biesbosch feed water are well within detection limit, except for PO₄, NO₂ and Cu with detection limits of 10, 100 and 1 µg/l, respectively. The composition of the MD permeate as well as the rejection of these components can be seen in Table 8.

Table 8. Standard deviation (σ), average and rejection of the MD permeate.

	pH	Cond.	NH ₃	SiO ₂	PO ₄	Cl	SO ₄	NO ₂	NO ₃	Br	
		µS/cm	mg/l	µg/l	µg/l	µg/l	mg/l	mg/l	mg/l	mg/l	
Average	5.99	4.2	0.3	14.2	<10	983.7	<0.1	<0.1	0.2	<0.1	
σ	0.18	3.3	0.1	6.2	0.0	864.0	0.0	0.0	0.2	0.0	
Rejection, %		99.1	-74.6	99.6		98.0			98.7		
	F	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC
	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
Average	<0.1	169.0	<0.8	1	1.6	126.0	21.1	242.5	1	1	86.9
σ	0.0	108.5	0.0	0.2	1.1	101.1	10.7	360.9	1	1	52.1
Rejection, %		99.7		2.7	94.5	97.8	99.7	99.3	51.2	83.4	96.4

As demonstrated, the MD has excellent rejection for most of the components. It is interesting to notice that the rejection improved significantly during the period where the system was operating uninterrupted for longer periods of time. This was especially true with the TOC measurement – during the startup period, while the system was not running stable, the TOC would measure at 200-300 µg/l, while when it was running stable the TOC was between 60 and 90 µg/l. The TOC of the permeate obtained with MD on Biesbosch meets the criteria for boiler feed water.

The reduced pH of the permeate can also be an explanation for the negative rejection of ammonia. The pH difference between the feed and the permeate side creates a vapor pressure difference for the ammonia, higher on the feed side, similarly to the membrane stripping process. Moreover, the ammonia will migrate to the permeate side due to temperature difference because it is volatile.

The main constituents of the permeate are therefore Na, Cl, Ca and K. Clearly the MD permeate needs further polishing if it is to be used as boiler feed water from a technology such as mixed bed resins, but due to the low conductivity, the load on the resins will be rather small. In fact, if the MD system is operated at higher fluxes, the rejection will also improve as shown by Abdallah et al [4].

Electrodialysis reversal

The EDR experiments on Biesbosch water were performed from 17 to 26th of October 2018 in continuous mode. The diluate was pumped a single time through the module and discharged, while the concentrate was continuously recirculated. The concentrate compartment conductivity is controlled by pumping out the concentrate and adding fresh feed to it to keep the conductivity below a certain setpoint. Prior to these experiments, the stack was cleaned from spacer clogging via disassembly and rinsing of the spacers under running water. During this cleaning, some of the membranes were cracked, which lead to slight water transport from the diluate to the concentrate compartment, which could be observed from the increasing level of the concentrate compartment. To counteract this phenomenon, the EDR was operated at lower water recovery in order to prevent the concentrate buffer tank from overflowing.

Although the EDR was operated with a 20 µm cartridge filter as a pretreatment, both the diluate and concentrate compartments exhibited increased pressure drops and the pressure increased from 0.7 to 0.9 bar for both channels at 120 l/h recirculation flow rate due to channel spacer fouling (the spacer thickness is 350 µm, thinner than the 700 µm spacer in the RO membrane module). On October 19, the EDR developed a severe leakage from the stack due to the increased pressure, which also brought it offline for three days. The bolts that clamp the module were tightened, which stopped the leakage and allowed operation to be resumed. Clearly, if the EDR is to be operated on Biesbosch, either thicker spacers need to be used or a more adequate pretreatment is needed, for example by using ultrafiltration membranes instead of cartridge filters. Better pretreatment is probably the safer application route compared to using thicker spacers, as these would increase the ohmic resistance of the stack.

A graph of the conductivities as a function of time can be seen in Figure 12.

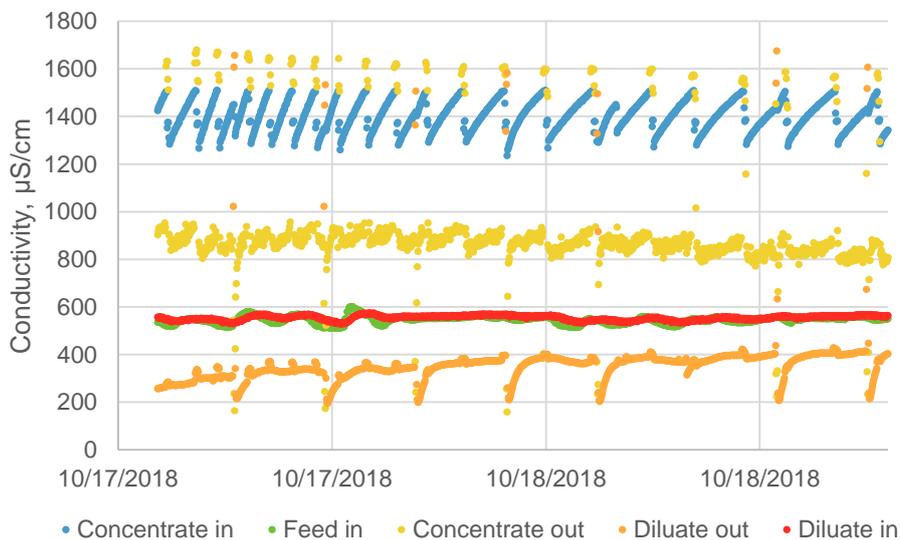


Figure 12. Conductivity (µS/cm) as a function of time, EDR

Feed in is the conductivity of the incoming water, diluate in and out is the conductivity of the diluate before and after passing the EDR module. Since the system is operated in continuous mode (single pass of the diluate through the module), the conductivity of the diluate in is almost the same as the incoming water. The concentrate in and out are the conductivity of the concentrate water before and after passing through the EDR module. In **Figure 12**, the conductivity of the concentrate outlet (around 900 µS/cm) is erroneous due

to horizontal mounting of the sensor which leads to the conductivity cell being dry, resulting in a lower reading. The correct reading should be around 1600 $\mu\text{S}/\text{cm}$, which is read only during pumping out of the concentrate when the sensor is completely submerged. The concentrate is continuously recirculated through the module until a certain maximum conductivity on the concentrate inlet is reached (1500 $\mu\text{S}/\text{cm}$), when concentrate water is being pumped out and replaced with fresh feed with lower conductivity.

What is interesting to notice in Figure 12 is that the diluate outlet concentration is very low immediately after reversal (performed for 5 minutes every 5 hours, which is probably not often enough) and then gradually increases in value. This suggests that concentration polarization is building on the solution-membrane interface, which is removed during reversal. To counteract this, the last day of operation was performed at 20 seconds reversal every 20 minutes, which reduced the average diluate compartment conductivity. However, online data is missing for this period due to a failed communication between the PLCs of the two containers.

As a reference, the laboratory results during the operation of the EDR for the diluate buffer tank (which are the same as feed water in continuous mode) can be seen in

Table 9.

Table 9. Composition of the EDR diluate buffer compartment (feed)

	NPOC	NH₃	SiO₂	PO₄	Cl	SO₄	NO₂	NO₃	Br	F
	mg/l	mg/l	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{l}$	mg/l	mg/l	mg/l	mg/l	mg/l
Average	2.0	0.3	3928	10.8	60800	53.4	<0.1	7.5	<0.1	0.2
σ	0.1	0.0	249	0.9	1200	1.2	0.0	0.2	0.0	0.0
	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC
	$\mu\text{g}/\text{l}$									
Average	49738	<0.8	1.0	31.1	6393	7004	37656	2.3	9.1	2402
σ	1171	0.0	0.1	9.6	133	142	633	0.1	1.1	204

It should be noted that the NO₂, Cr, Br and Cu are at their detection limits, while the PO₄ is very close to detection limit of 10 $\mu\text{g}/\text{L}$. The concentration after single pass operation of the EDR stack can be seen in Table 10.

Table 10. Composition of the treated water after EDR (diluate outlet)

	NPOC	NH₃	SiO₂	PO₄	Cl	SO₄	NO₂	NO₃	Br	F
	mg/l	mg/l	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{l}$	mg/l	mg/l	mg/l	mg/l	mg/l
Average	2.0	0.6	3950	10.2	38200	43.6	<0.1	4.5	<0.1	0.2
σ	0.1	0.1	198	0.4	7400	3.7	0.0	1.0	0.0	0.0
Rejection (%)	-1.2	-103.9	-0.6	6.2	37.2	18.4		40.8		22.6
	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC
	$\mu\text{g}/\text{l}$									
Average	31522	<0.8	<1	26.9	5611	4893	34457	2.1	4.7	2388
σ	10734	0.0	0.0	8.6	773	1421	4364	0.1	0.4	265
Rejection (%)	36.6			13.5	12.2	30.1	8.5	5.2	48.1	0.6

In this case the EDR does not remove any organics, which can be seen in the values of both the NPOC and the TOC measurements, suggesting that the TOC was not charged. Interestingly, while the EDR removed considerable amounts of the Cl, SO₄, NO₃, Ca and Mg, the rejection for Na and K was very poor. Ionic balance will be done to further investigate this preferential rejection. The EDR also does not reject any silica, which is expected since it is not charged. The negative rejection of ammonia is also interesting, but it should be kept in mind that the measured values are close to the detection limits.

The EDR was operated at 95% recovery, considering the refilling of the concentrate compartment. The average diluate conductivity was 384 µS/cm while the average diluate inlet conductivity was 555 µS/cm or an average rejection based on conductivity of 31%. The EDR stack had 20 cell pairs (5 were already removed due to breakage during cleaning) and was operated at 39 V, resulting in an average current of 0.17 A. While the conductivity removal is not very high, it can be further improved by performing a more frequent reversal. Moreover, the low power consumption of the stack should also be considered.

The stack was producing an average of 120 l/h diluate, with an average desalination power of 6.6 W or 0.055 kWh/m³ of diluate. This makes the EDR a potentially interesting technology for reducing the load on the ion exchange unit of the plant for production of demineralized water. The average pressure drops for the diluate and concentrate channels are 0.8 and 0.6 bar, respectively. Considering the average flow rates of 125 l/h, the specific pumping power can be calculated to 0.041 kWh/m³.

Therefore, the sum of the pumping and desalination energy needed to produce 1 m³ of diluate at 31% conductivity removal was 0.096 kWh/m³.

b) F200 process condensate case

The F200 stream is received in the water treatment unit of BASF after treatment with granular activated carbon (GAC). After receiving the water, it is treated with rapid sand filtration, which can be aerated if needed. The stream contains on average 50 µg/l of iron, therefore the aeration can change the oxidation state of the iron from the water soluble ferrous iron (+2) to the water insoluble ferric iron (+3), which is known to be very problematic for membrane processes and RO in particular, since it causes fouling on the front end of an RO module [6]. Therefore, throughout the tests, the aeration of the sand filter was disabled. The insoluble ferric iron is also known to cause biofouling by enabling the growth of iron reducing bacteria [6].

Previous analysis of the F200 process water performed by BASF showed that a large part of it is composed of low molecular weight neutrals, which cannot be retained by ion exchange process (Table 11).

Table 11. LC-OCD Composition of the F200 stream before GAC treatment

Date	Unit	09-05-17	23-05-17
DOC - Dissolved	µg/l C	252	467
DOC - CDOC, hydrophilic	µg/l C	252	467
CDOC - Bio-polymers	µg/l C	7	6
CDOC - Bio-polymers - DON	µg/l N	5	<1
CDOC - Bio-polymers - N/C	µg/µg	0.69	
CDOC - Building Blocks	µg/l C	20	18
CDOC - LMW Neutrals	µg/l C	218	438
CDOC - LMW acids	µg/l C	8	5
SUVA (SAC/DOC)	l/(mg*m)		0.23

As seen in Table 12, the GAC treatment greatly reduces the low molecular weight neutrals.

Table 12. LC-OCD analysis of the F200 composition after GAC treatment

Date	Unit	12-10-16
DOC – Dissolv.	µg/l C	164
DOC - CDOC, hydroph.	µg/l C	164
CDOC - Bio-polym.	µg/l C	6
CDOC – Build. Blocks	µg/l C	6
CDOC - LMW Neutr.	µg/l C	152
Inorg. Colloidal (SAC)	m-1	0.06
SUVA (SAC/DOC)	l/(mg*m)	0.49

Typically, the F200 stream is composed of acetone, isopropanol and t-butanol.

The lab analysis for the first period of running the containers on F200 can be seen in **Table 13**.

Table 13. Lab analysis of the F200 feed water 22/8 to 27/8

Mix 1	pH	Temp	Cond	NPOC	NH ₃	SiO ₂	PO ₄	Cl	SO ₄	NO ₂	NO ₃	Br
			µS/cm	mg/l	mg/l	µg/l	µg/l	µg/l	mg/l	mg/l	mg/l	mg/l
Average	8.1	28.2	48.2	0.7	8.0	10.8	17.3	<100	<0.1	<0.1	<0.1	<0.1
σ	0.0	0.7	1.6	0.1	0.3	0.9	15.1	0.0	0.0	0.0	0.0	0.0
	F	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC	
	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	
Average	<0.1	54.7	<0.8	3.1	50.8	70.8	29.2	34.2	<1.0	<1.0	545.0	
σ	0.0	10.9	0.0	4.6	1.6	6.7	6.7	14.8	0.0	0.0	65.5	

During the second period, the composition was similar, see Appendix A.2 Composition of the F200 for the November period.

Reverse osmosis

RO was applied to the F200 process stream for two periods – from 22/08 to 27/08 and from 9/10 to 15/10. In the first case it was operated at 75% recovery and 20 l/(m².h) flux with a dosing of 3.3 mg/l antiscalants.

During the second run it was operated at 85% recovery and 25 l/(m².h) flux and no dosing of antiscalants. The laboratory results from the second period of running can be seen in Table 14.

Table 14. RO permeate quality from the second run on F200

	Cond.	NH ₃	SiO ₂	PO ₄	Cl	SO ₄	NO ₂	NO ₃	Br	F
	μS/cm	mg/l	μg/l	μg/l	μg/l	mg/l	mg/l	mg/l	mg/l	mg/L
σ	1.2	0.34	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Average	11.2	2.35	<10	<10	<100	<0.1	<0.1	<0.1	<0.1	<0.1
Rejection (%)	79.1	73.5								
	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC
	μg/L	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l
σ	0.0	0.0	0.0	0.4	2.1	4.0	72.9	0.0	0.0	25.9
Average	<10	<0.8	<1.0	1.2	15.5	6.5	120.5	<1	<1	103.8
Rejection (%)				97.7	82.3	48.4	-71.7			78.5

The composition of the RO permeate during the first run was similar, except for iron of 16 μg/l, and Sodium of 62 μg/l.

The poor rejection of ammonia is expected at this relatively high pH, since some of it is in the volatile NH₃ form and cannot be rejected by RO. However, there is no simple explanation for the high concentration of sodium in the RO permeate. During the first period, the sodium measured in the incoming water was 34.2 μg/l, while in the RO feed buffer tank it was 563 μg/l (over 16 times higher). While the RO feed buffer tank is somewhat concentrated due to the partial concentrate recirculation, the rise in the conductivity is only 69%, compared to the incoming water. Therefore, it is unlikely that the high sodium concentration in the RO buffer tank is only due to concentration induced by the recirculation of concentrate and is probably coming from an external source. The most probable source is the added antiscalant (added at 3.3 mg/l). While the exact composition of the Nalco Permatreat 191T is a trade secret, some other popular antiscalants contain sodium, e.g. sodium hexameta-phosphate (SHMP). The sodium concentration in the RO buffer tank during the run without antiscalants is much lower at 148 ±66.4 μg/l, confirming the possibility that sodium is coming from the antiscalant. The sodium concentration was also measured online via a sodium meter (Swan, Switzerland), which is expected to be a more reliable measurement, since less contamination is expected due to the nature of the online measurement. This showed that an average concentration of sodium in the RO permeate of 56.9 μg/l during the first run and 3.36 μg/l during the second run.

The antiscalant used in the first testing period is known to be of the organo-phosphonate group [7], which can explain the negative rejection of PO₄ in the RO permeate, i.e. the antiscalant added to the feed probably degraded to orthophosphate [8] and some of it managed to pass the membrane.

The online cation conductivity, degassed conductivity and sodium during the second run can be seen in Figure 13.



Figure 13. Online measurement of the cation conductivity, degassed cation conductivity and sodium during the second run in the RO permeate

The cation conductivity and degassed cation conductivity are important parameters for the quality of the boiler feed water. The cation conductivity is measured using an online meter (Swan, Switzerland), by running the water over a cation exchange resin bed, which replaces the cations with protons. Therefore, after the resins, the water is more acidic and this step typically acts as a conductivity multiplier. In our specific case, however, the major constituent in the water is ammonia, so the cation conductivity is in fact lower than the specific conductivity (Table 14), since the pH is reduced and becomes more neutral and less conductive after the resins.

After passing the cation exchange resins, the water is run through a boiler at a temperature just below the boiling point of water, which removes the volatile components, and what is left is the degassed cation conductivity. There is a large difference between the cation conductivity (c.a. 2 $\mu\text{S}/\text{cm}$) and the degassed cation conductivity (c.a. 0.17 $\mu\text{S}/\text{cm}$), which suggests that there are a lot of carbonates in the stream, which are removed by degasser boiler.

To meet the boiler feed water standards, the degassed cation conductivity should be below 0.2 $\mu\text{S}/\text{cm}$. This goal was met most of the time, except for small peaks, which are probably glitches due to instable flow over the sensor and consequently unstable temperature control of the boiler temperature.

While there was no problem with the permeate quality of the RO, there was a severe problem with feed channel spacer clogging (see Figure 14)

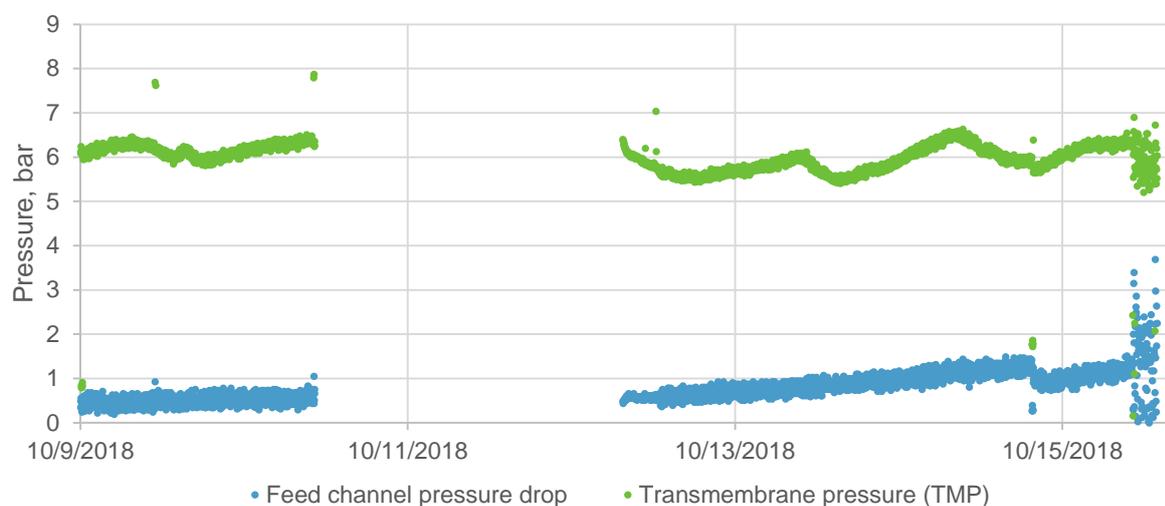


Figure 14. Feed channel pressure drop (blue) and trans membrane pressure (TMP, green) during the second RO run

As seen in the figure, the process started with a feed channel pressure drop of around 0.4 bar, and ended at over 1 bar towards the end of the experiments. Similar behavior was seen in the first run, but then the feed channel pressure drop increased to over 2.5 bar. This increase is not acceptable over such short periods. It should be noted that the problem was mainly related to feed channel pressure drop and not the transmembrane pressure. The fouling is probably due to biofouling with iron reducing bacteria, as discussed on page 24. The presence of iron can cause problems with biofouling due to both iron reducing bacteria in the anaerobic zones as well as iron oxidizing bacteria in the zones with excess oxygen. During the runs on F200, floating orange flocks could clearly be seen attached on the sides of the buffer tanks, that also settled on the piping. One of the flow meters of the installation was fouled toward the end of the experiments, which explains the oscillating pressure. This problem also happened during the first run on F200.

The feed spacer fouling was not reversible using the flush in the opposite direction with bubbles (air scouring), followed by water flush (**Figure 14**). Also, an attempted cleaning in place with HCl at pH 2, followed by NaOH at pH 12, did not resolve the problem with feed spacer fouling. Better results can be expected from cleaning in place with citric acid (used for iron chelation), elevated temperature and surfactants, however this was not attempted in these experiments.

The flocks coming after the sand of BASF can be seen on Figure 15, the resulting fouling on the RO cartridge filters can be seen on **Figure 16**.

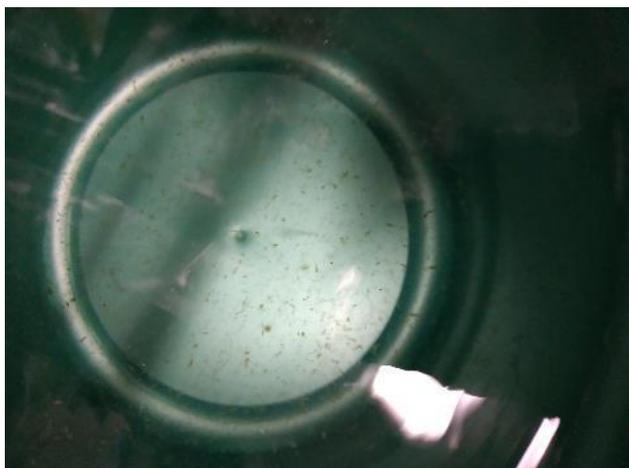


Figure 15. Flocks coming with the F200 stream after the sand filter of BASF



Figure 16. Fouling on the cartridge filters caused by F200

While the flocks are clearly larger than the pore size of the cartridge filters (60 μm), it is possible that they break down over time to smaller ones that pass the filters and end up inside the RO module. It is recommended to take a sample of the flocks in the F200 and study their origin, which will allow a better design of the pretreatment installation.

A basic membrane autopsy was performed on the module to investigate the problem further. Although the autopsy was done after running the system for 2 weeks on another stream (Biesbosch with MCA without bisulfite neutralization), the pressure drop of the feed spacer channel remained high and the feed spacer was still fouled. A visual representation of the beginning (**Figure 17**) and the end (**Figure 18**) of the feed spacer channels can be seen below. An analysis for metals was also performed, revealing the presence of iron. Unfortunately, microbiological analysis could not be done, since it would not be representative because of running multiple streams through the module.



Figure 17. Visual inspection of the inlet cap and beginning of the feed channel



Figure 18. Visual inspection of the outlet cap and end of the feed channel

Clearly the beginning of the feed spacer is more fouled than the end, but interestingly the inlet cap is much cleaner than the outlet cap. This suggests that the fouling material was smaller before entering the module, grew on the spacer strands, and then part of it detached and reattached at the outlet cap of the module.

The average transmembrane pressure in the first period was 4.47 bar with channel pressure drop of 1.55 bar and the average transmembrane pressure in the first period was 5.98 bar with a channel pressure drop of 0.79 bar. The higher transmembrane pressure during the second period can be explained by the higher recovery (85%) as well as 25 l/m².h flux instead of 20 l/m².h during the first period at 75% recovery. The average specific energy consumption for both periods, including the feed channel pressure drop as well as the transmembrane pressure and assuming 100% pump efficiency, is 2.75 kWh/m³.

In order to better understand the process, the RO mass transfer coefficient and spacer pressure drop were normalized using the equation in Appendix A.4 Used equations.

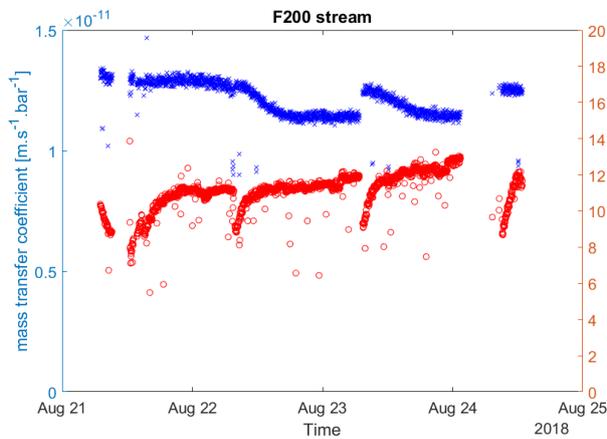


Figure 19. Normalized mass transfer coefficient and salt passage for the first period of F200

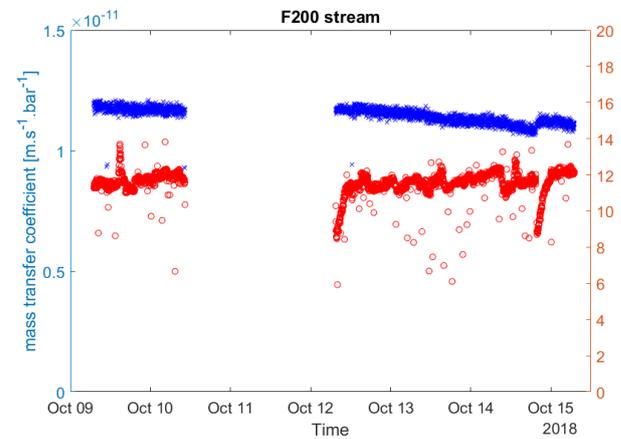


Figure 20. Normalized mass transfer coefficient and salt passage for the second period of F200

As seen in **Figure 19** and **Figure 20** for both periods, there seems to be a rapid decline in the membrane mass transfer coefficient as well as an increase in the normalized salt passage. This shows that the (bio)fouling is not limited to only the feed spacer but blocks some of the active membrane area as well. The mass transfer coefficient reduction is also evident for the second period of operation but at a much lower scale.

The very small increasing trend for normalized salt passage is concerning, however it should be noted that it is derived based on the conductivity and most of the conductivity of the F200 stream is due to ammonia which easily passes the membrane at higher pH. Therefore, a simple slight increase of the pH could cause this trend. It is also possible that the system was still not stabilizing, since the RO buffer tank starts with a feed concentration and gets concentrated from the recirculation from until it reaches equilibrium.

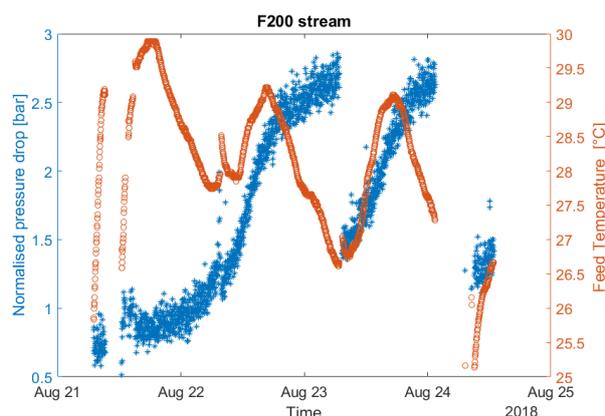


Figure 21. Normalized feed channel pressure drop and temperature for the August period

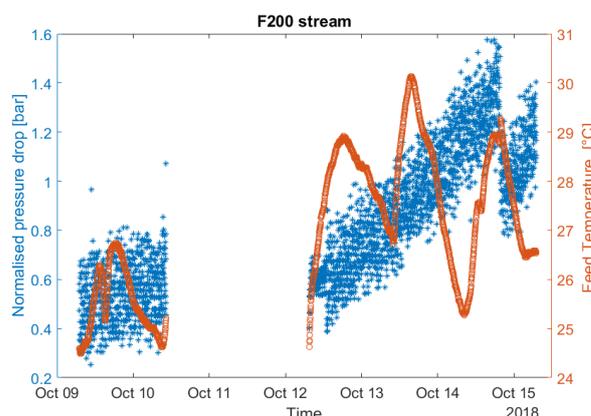


Figure 22. Normalized feed channel pressure drop and temperature for the October period

During both periods the feed channel pressure drop sharply increased, due to the feed spacer fouling. Such sharp increase is not normal for RO operation and better pretreatment of the feed water is necessary.

Overall, this technology performed very well in terms of permeate quality on F200. However, it should be noted that some of the components that can be periodically present in this stream, such as methanol, are typically poorly rejected by RO. Better pretreatment of the feed is needed to prevent feed spacer fouling. The current pretreatment with rapid sand filtration starts to release flocks after 2-3 days of operation, so it is possible that with a stricter control of the backflushing cycles, sand filtration can also be sufficient. UF is likely to also have problems if indeed the problem is with Fe^{3+} and iron reducing bacteria. It should be noted however, that possibly all problems with iron could be avoided if the containers are modified to avoid the contact of water with air and minimize the formation of Fe^{3+} ions.

Membrane Stripping

Membrane stripping was applied from 9th to 16th of October with the intention to reduce the ammonia load. The pH on the feed side was targeted to be around 10 and was maintained by an automatic dosing of NaOH to keep the ammonia volatile. The pH on the distillate side was targeted to be around 2 and was maintained by automatic addition of HCl to keep it in the non-volatile NH_4^+ form. Typically, to intensify the process, the temperature is maintained at 50-60 °C on both sides of the membrane. However, since both electrical heaters were broken at the time of the experiments, the membrane stripping experiments were conducted at inflow temperatures of around 10-15 °C. The main performance parameters of the stripping process can be seen in Figure 23.

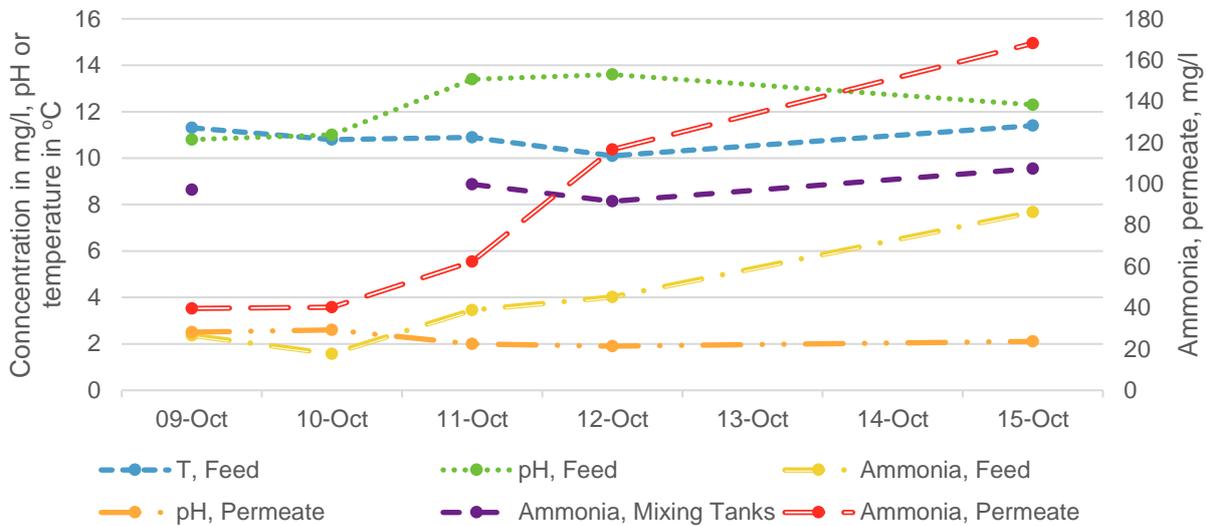


Figure 23. Performance of the membrane stripping process. Temperature in degrees Celsius, concentrations in mg/l. Except for ammonia on the permeate side, all other parameters are on the primary, left axis.

The feed buffer side of the MS process is the one that is being stripped of ammonia while being kept at high pH, and the permeate buffer side is enriched with ammonia at low pH. The “inlet water” is the concentration of incoming feed stream containing ammonia and is used as make-up water for the feed buffer tank (see Figure 4).

The process was operated in batch mode, i.e. the ammonia accumulates inside the permeate buffer tank, increasing over time until the solution is manually replaced (this replacement was never done during the testing period, hence, the accumulation of ammonia in the permeate buffer). As seen in **Figure 14**, as the ammonia concentration on the permeate side increased, the concentration on the feed side also increased, reducing the removal efficiency. Towards the end of the experiment, almost no ammonia was removed from the stream. It is interesting to notice that the membrane seems to have been wetted before the experiments were started. From the beginning of the experiments, a flow of around 50 l per day can be seen from the permeate compartment, that needed to be refilled (**Figure 24**). It is safe to assume that the solution was slowly transported from the permeate to the feed side via wetted areas of the membrane, reached the low-level value set for the tank of 80 l and it was refilled to 85 l with demineralized water.

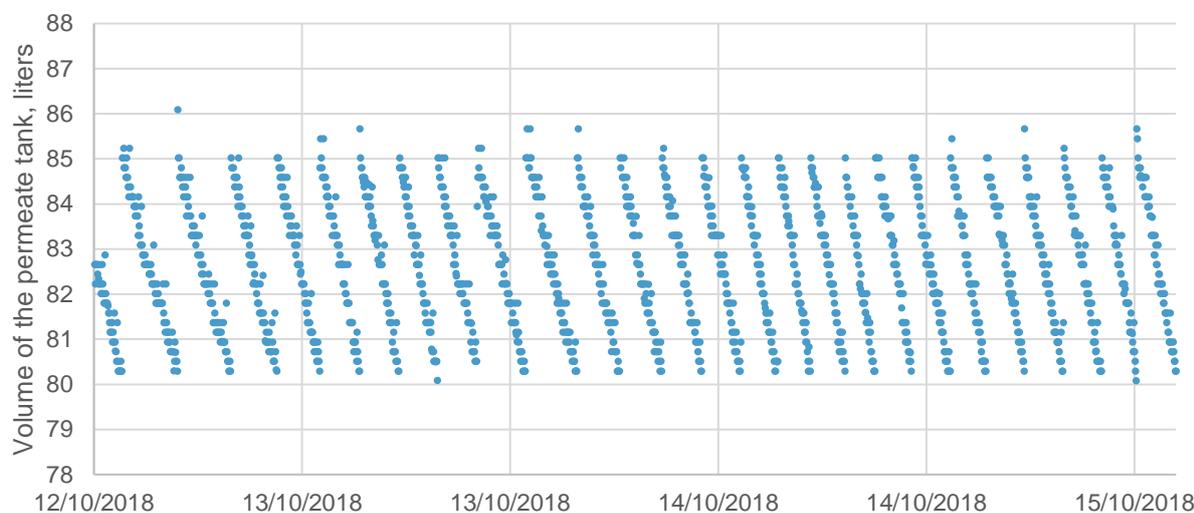


Figure 24. Volume of the permeate compartment during membrane stripping

While it cannot be confirmed that the water passing the membrane ended up in the feed (because of low sampling frequency of the water level and large volume of incoming water), the other possibility is that the water simply leaked out from the permeate compartment. Such leak was not observed, therefore it is more likely that the water went from the permeate side, through the membrane and into the feed compartment.

Membrane wetting is an unwanted process in MS and MD, whereby the pores of the hydrophobic membrane become wetted due to either excessive hydraulic pressure, membrane scaling, (bio)fouling or the presence of surfactants or other components that can reduce the surface tension or a combination of these factors.

The streaming process began with removing most of the ammonia and leaving around 2 mg/l of ammonia in the feed water (Figure 23). During the following days, the ammonia concentration inside the feed continued to increase and at the final days it reached 8 mg/l, which is close to the mixing tank concentration. It is likely that as the concentration of ammonia on the permeate side increased, some of the water transported through the wetted regions of the membrane together with the stripped ammonia ended up back inside the feed compartment, reducing the removal efficiency and eventually leading to an equilibrium.

The hydraulic pressure drop was 0.31 and 0.14 bar on the feed and permeate sides, respectively. The higher pressure on the feed side was caused by a cartridge filter slightly clogged scaling coming from the electric heater. The skid was producing 30 l/h of water with stripped ammonia. At a recirculation flow rate of 600 l/h, the specific pumping energy needed to produce one cubic meter of water with stripped ammonia is 1.58 kWh/m³, assuming 0.14 bar pressure drop for both channels.

c) General condensate stream

The condensate that was treated inside the containers is a mixture of all returning condensates from the plant and is reused as boiler feed water after polishing with a mixed bed. During the tests, the ammonia was the main component above the detection limit. In accordance with the F200 stream, the ammonia is added by BASF as an alkalizing agent to reduce corrosion risk. However, treating the condensate directly with the MB leads to the cation resins being saturated quickly by the ammonia. Several technologies were tested on

this stream – mixed bed, a combination of strong acid cation (SAC) resins followed by mixed bed, reverse osmosis and electro dialysis.

The lab analysis of the mixed condensate stream can be seen in Table 15.

Table 15. Composition of the feed stream, condensate

Mix 1	pH	Temp.	Cond.	NH ₃	SiO ₂	PO ₄	Cl	SO ₄	NO ₂	NO ₃	Br
		°C	µS/cm	mg/l	µg/l	µg/l	µg/l	mg/l	mg/l	mg/l	mg/l
Average	8.3	27.6	11.0	2.3	<10	11.7	<100	<0.1	<0.1	<0.1	<0.1
σ	0.5	3.3	0.1	0.2	0.0	2.3	0.0	0.0	0.0	0.0	0.0
	F	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC
	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	ppb
Average	<0.1	12.3	<0.8	<1.0	2.9	<10	2.6	10.9	<1.0	<1.0	56.3
σ	0.0	8.5	0.0	0.0	3.0	0.0	1.7	2.6	0.0	0.0	12.4

Most of the components are below their detection limits. It should be noted that PO₄, Ca, Fe Mg and Na are also very close to their detection limit of 10, 10, 1, 2 and 10 µg/l, respectively. The TOC in the condensate is also very low at an average of 56 µg/l, while the limit of the BASF plant was 250 µg/l for reuse as boiler feed water. The main component causing the high raw conductivity of the stream (11 µS/cm) is ammonia, since the cation conductivity is 0.88 µS/cm and the average degassed cation conductivity is 0.23 µS/l.

The degassed cation conductivity, sodium and silica were monitored online for a short period (see Figure 25).

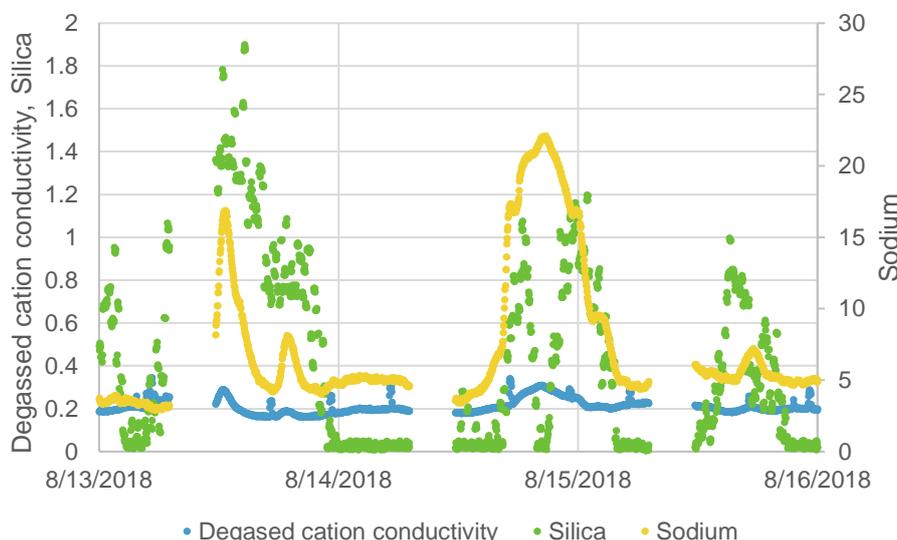


Figure 25. Degassed cation conductivity (µS/cm), silica (µg/l) and sodium (µg/l)

The degassed cation conductivity was very close to the imposed limit of 0.2 µS/cm. However, most of the time it was somewhat higher and this is the only measurable parameter of the condensate that prevents it from being reused as boiler feed water. The silica is mostly stable at values below 2 µg/l. The sodium was also quite low at normal values around 5 µg/l and spikes just over 20 µg/l.

Since the quality of the condensate was very good, separate experiments were conducted where sodium, chloride, silica and sulfate were added to the stream aiming at 0.1 mg/l concentrations, simulating a condensate with lower quality.

Reverse osmosis

Reverse osmosis was applied on the condensate stream in two periods 30/07 to 21/08 and 03/09 to 28/09 with 85% recovery and 25 l/(m².h) flux, without addition of antiscalants. The lab results for these periods can be seen in Table 16.

Table 16. Lab results of the RO permeate on condensate water for the period 30/07 to 21/08

RO	Cond.	NH ₃	SiO ₂	PO ₄	Cl	SO ₄	NO ₂	NO ₃	Br	F
	μS/cm	mg/l	μg/l	μg/l	μg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Average	10.7	2.1	<10.0	11.1	<100.0	<0.1	<0.1	<0.1	<0.1	<0.1
σ	0.6	0.1	0.0	1.6	0.0	0.0	0.0	0.0	0.0	0.0
Rejection (%)	2.7	9.2		5.3						
	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC
	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	ppb
Average	30.3	<0.8	<1.0	2.5	<10.0	2.4	12.6	<1.0	<1.0	40.9
σ	32.3	0.0	0.0	3.6	0.0	1.2	3.9	0.0	0.0	7.2
Rejection (%)	-145.7			15.0		9.5	-14.9			27.4

It is not so straight-forward to interpret the lab results as most of the components are very close to their detection limits. It should be noted that at these low levels, sample contamination, contamination during measurements as well as sample cross contamination are very hard to avoid. The low rejection of the ammonia, the main component measured in the stream can be explained by the relatively high pH of the stream (pH 8.3), which keeps ammonia in the volatile NH₃ form, which is not rejected by RO. The low rejection based on conductivity can also be explained by the low rejection of ammonia. PO₄ is very close to its rejection limit of 10 μg/l. Calcium has a negative rejection of -146%, but it should be noted that calcium was measured in the permeate only during the first 5 days, possibly washing off some residual membrane scaling (e.g. CaCO₃) from previously running the system on Biesbosch water. For the remaining 14 days, calcium was below its detection limit of 10 μg/l. The measurement for Fe and Mg has a large standard deviation and should be noted that the values are very close to their detection limit of 1 μg/l.

It is noteworthy that the sodium is negatively rejected (-15 %), however, it has a very good standard deviation, compared to the average value. Sodium has a very small atom, so it is possible that it passes the membrane to keep the electroneutrality condition. This would be likely if a negatively charged ion is passing the membrane, however, the major component found in the permeate is ammonium, which is positively charged. Alternatively, at neutral and high pH, the RO membranes have a negative charge, that can attract the positively charged sodium ion, increasing its concentration at the membrane-water interface. It can later diffuse to the lower concentration in the RO permeate.

Interestingly, the RO rejects only about 30% of the TOC on condensate, whereas it had 98% rejection for the TOC composition on Biesbosch.

Overall, the rejection of RO for most of the components was quite poor, compared to operating it on Biesbosch water.

Since most of the components in the lab results are too low to be measured accurately, the online conductivity and sodium meters (Swan, Switzerland) were connected to the RO permeate during the second period of running RO on condensate water 21/08 to 3/09 (Figure 26).

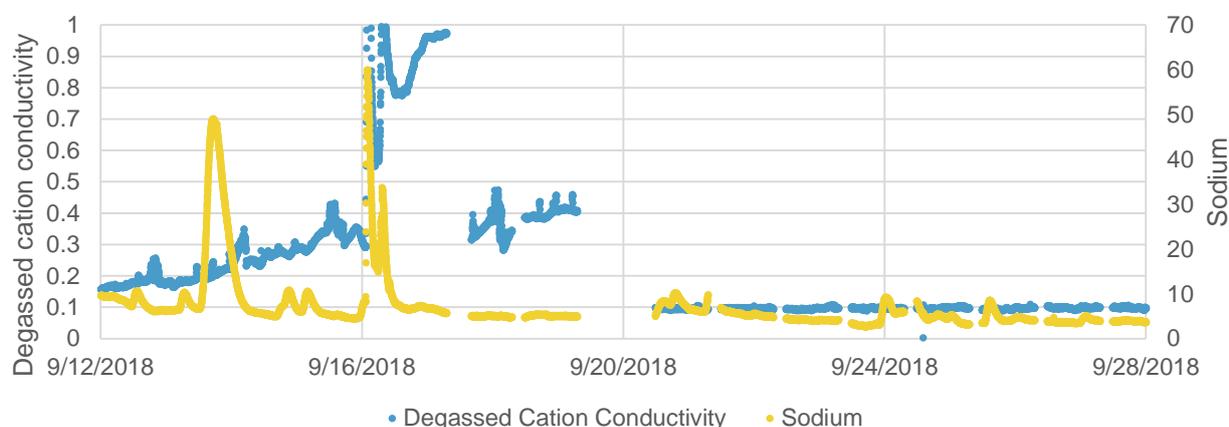


Figure 26. Online measurements of the RO permeate on condensate, degassed cation conductivity ($\mu\text{S}/\text{cm}$) and sodium ($\mu\text{g}/\text{l}$)

This figure can be interpreted in two parts – before and after 20/09. The first part of the graph was done with an old membrane that had feed spacer fouling due to previously being operated on F200. Throughout the experiments, the degassed cation conductivity kept increasing. To investigate the problem, the cation exchange resins on the degassed cation conductivity meter were changed, which reduced the cation and degassed cation conductivities, but did not bring them to boiler feed water specifications. To investigate if membrane damage was the cause of the rising degassed cation conductivity, the membrane was replaced on 19/9 and since then, the permeate quality greatly improved. However, this is probably a coincidence and the bad RO permeate quality was probably due to bad feed condensate quality. Although the membrane had feed spacer fouling from the F200 stream, this should not affect the permeate quality.

On the 18/09, when the degassed cation conductivity was at its peak, the PO_4 measured in the feed water (mixing tanks) was also the highest recorded at $66 \mu\text{g}/\text{l}$, on all other days it was below detection limits. Similarly, on 17/09, the chloride concentration was $300 \mu\text{g}/\text{l}$, and on all other days it was below the detection limit of $100 \mu\text{g}/\text{l}$. While the degassed cation conductivity looks very good for the period with the new membrane, it should be noted that during most of the time, the raw condensate also has a degassed cation conductivity of around $0.2 \mu\text{S}/\text{cm}$ (Figure 25).

Interestingly, there are no peaks in the sodium for the period with the new membrane after 20/09 and before that, two peaks of over $50 \mu\text{g}/\text{l}$ can be observed. While there is no reason to believe that the membrane suffered damage, it is certainly possible. However, if we look at the peaks of sodium in the condensate (Figure 25), the feed sodium has peaks of over $20 \mu\text{g}/\text{l}$. Therefore, if the peaks in the permeate were due to damaged membrane, it would have to be completely destroyed to have peaks over $50 \mu\text{g}/\text{l}$, which is certainly not the case.

Ideally, two sets of online meters should be monitored, one on the feed water and one on the RO permeate. This would be a valuable improvement of the containers in future tests.

If indeed the RO permeate quality was bad due to variations in the condensate water quality, the application of RO on this stream should be further studied. An LC-OCD sample of the feed stream and the RO permeate

streams would be very beneficial to reveal the composition of the system, however such sample was not taken at the time.

To simulate bad quality condensate, a solution containing Na, Cl, SO₄ and SiO₂ was continuously spiked into the mixing tanks. The result of the experiment can be seen in Figure 27.

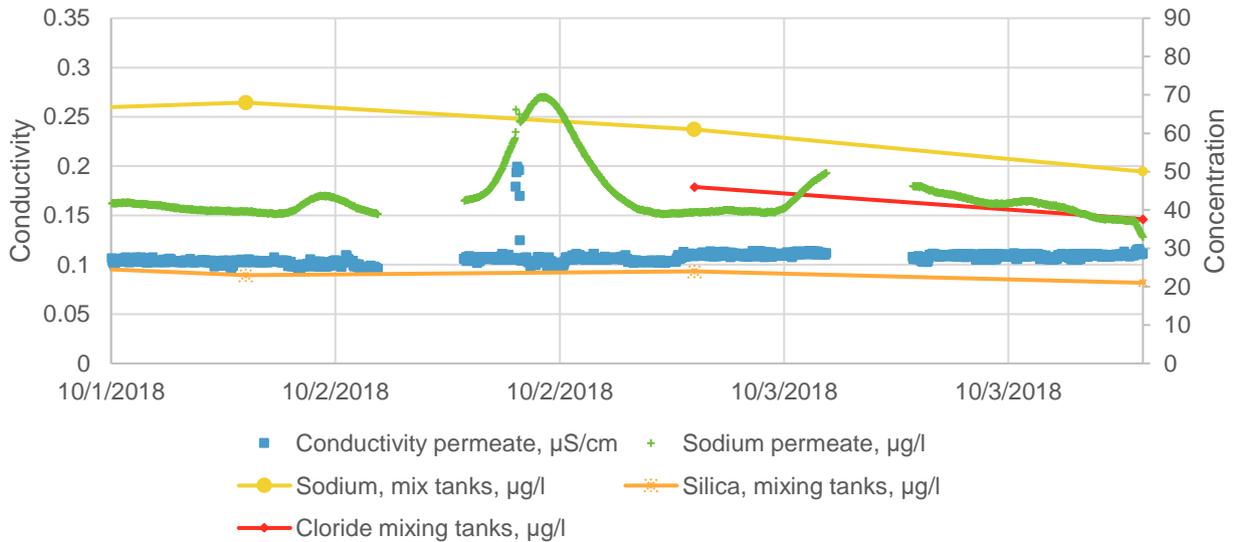


Figure 27. Spiking experiments, mixing tanks feed concentration, RO permeate concentration and conductivity

The conductivity and the sodium inside the permeate were measured with online instruments, the rest of the concentrations were measured with grab samples in the lab of BASF. The chloride and silica were below their respective detection limits of 5 and 10 µg/l in all samples taken from the permeate (special, low detection limit tests were done in this case for chloride). This results in rejections of chloride and silica higher than 88 and 58%, respectively, however these rejections are probably much higher, which is masked by the detection limit being close to the measurements. The SO₄ was below the detection limit of 0.1 mg/l in both the mixing tanks and the permeate, so it is not conclusive how well it was rejected. Similarly to the test with normal condensate, the sodium was very poorly rejected at 24% average rejection. The spike in the sodium permeate (grab samples), higher than the sodium in the feed (online measurement) can be explained by the lower sampling frequency of the sodium in the mixing tanks, possibly in this period the sodium in the feed water was elevated.

The low sodium rejection results were also confirmed with a grab sample analysis in the Swan Sodium online meter, which showed about 40% rejection of the feed sodium inside the mixing tanks, compared to the RO permeate.

The normalized membrane mass transfer coefficient, salt passage and feed channel pressure drop can be seen in **Figure 28** and **Figure 29**:

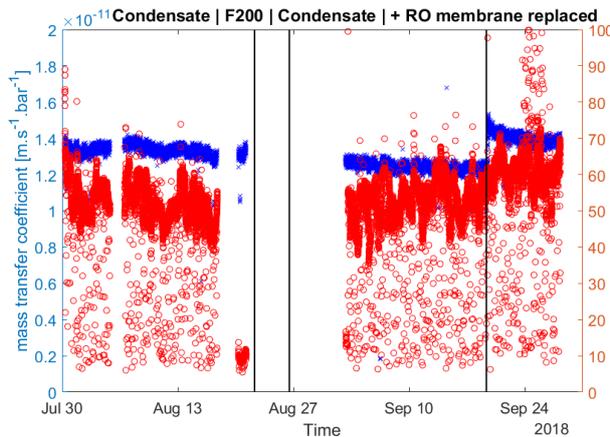


Figure 28. Normalized membrane mass transfer coefficient and salt passage for the condensate stream

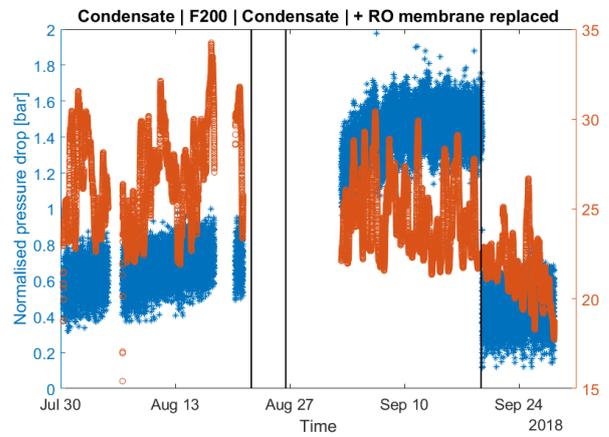


Figure 29. Normalized feed channel pressure drop and temperature for the condensate streams

Overall the operation of the RO on condensate water seems very stable in terms of membrane mass transfer coefficient as well as salt passage. Although the mass transfer coefficient seems to slowly decrease, this decrease is most likely reversible. The feed spacer channel seems to slightly increase, probably due to the cellulose fibers found in this stream, but they should be soluble in a basic cleaning in place in case this is needed. The sharp increase in the feed channel pressure drop after August 27 is due to fouling from running the RO on the F200 stream.

The average transmembrane pressure with a new membrane was 5.9 bar with feed channel pressure drop of 0.4 bar at 85% recovery and 25 (l/m².h) flux (or 217.5 l/h produced permeate). The average specific energy consumption, including the recirculation flow and assuming 100% pump efficiency is 2.14 kWh/m³.

Mixed bed

The general condensate stream was treated with MB during the period of 30/07/2018 until 21/08/2018, the production flow was around 275 l/h. During the treatment period no silica nor sodium was found in the MB effluent. The TOC concentration and conductivity of the MB effluent are given in Figure 30.

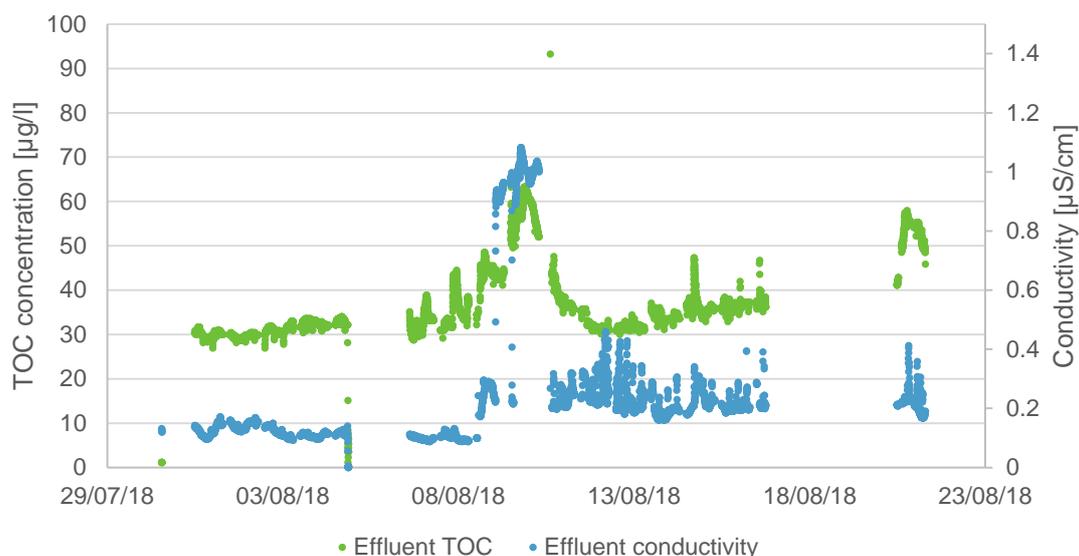


Figure 30. The TOC concentration and degassed cation conductivity of the MB effluent during the condensate stream treatment.

The overall TOC concentration was lower than 50 ppb, and the degassed cation conductivity below 0.4 $\mu\text{S}/\text{cm}$. The increase in both parameters around the 8th of August was due to exhaustion of the MB resins. The resins were replaced on the 9th of August and both parameters were within expectations again. The first ion that broke through was ammonia, which explains the reasoning to put an SAC in front of the MB in order to decrease the amount of regeneration needed for the complete MB. The ionic analyses for the MB effluent are given in Table 17 .

Table 17. Lab results of the MB effluent on condensate water for the period 30/07 to 21/08.

	Cond.	NH ₃	SiO ₂	PO ₄	Cl	SO ₄	NO ₂	NO ₃	Br	F
	$\mu\text{S}/\text{cm}$	mg/l	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{l}$	mg/l	mg/l	mg/l	mg/l	mg/l
Average	-	< 0.05	<10.0	<10.0	<100.0	<0.1	<0.1	<0.1	<0.1	<0.1
σ	-	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC
	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{l}$	ppb
Average	<10	<0.8	<1.0	<1	<10.0	<2	<10	<1.0	<1.0	36.2
σ	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.0

Based on the ionic analyses, it is clear that the MB mainly removed the general cations and anions as all values are below their respective detection limit. Except the TOC removal is low in absolute value, as less than half of the TOC is removed (35.70 %) from the condensate stream, but the incoming TOC concentration of the condensate was already very low (around 56 ppb). Despite the low TOC removal efficiency, the TOC concentration in the effluent is more than low enough in order to make reuse possible.

SAC followed by mixed bed

The treatment of the condensate stream with the SAC resin followed by the MB was conducted from 03/09/2018 till 27/09/2018. In **Figure 33**, the conductivity for the feed water and SAC effluent and the TOC concentration for the MB effluent are given.

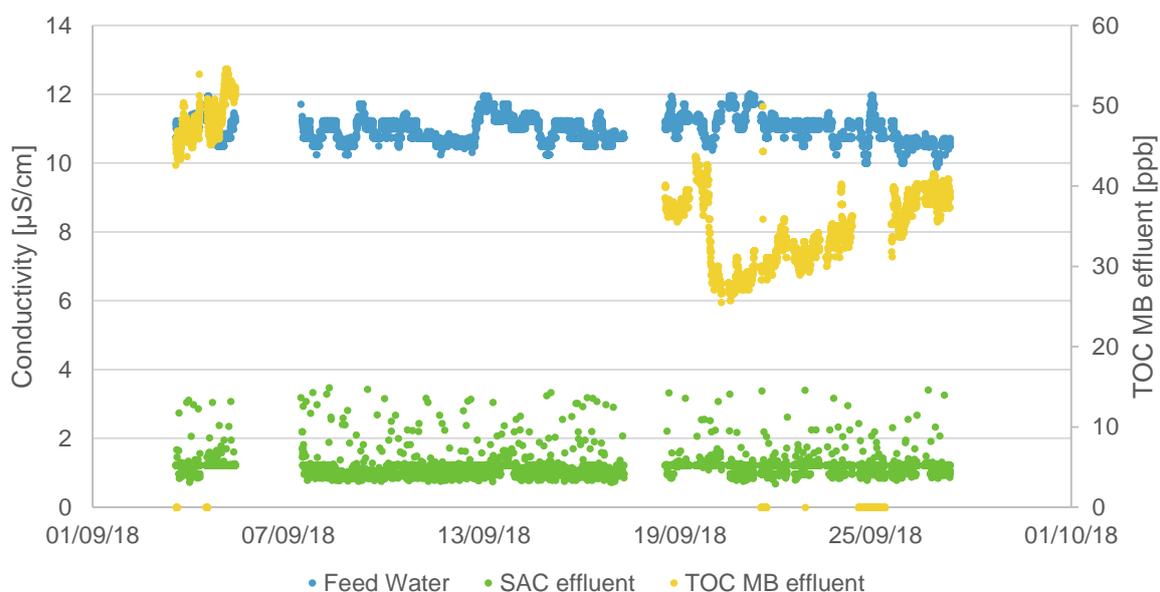


Figure 31. The TOC concentration of the MB effluent and conductivity of the feed water and SAC effluent during the condensate stream treatment.

The normal conductivity meter of the MB effluent is not given as the conductivity transmitter was broken during the testing period, however, the average degassed cation conductivity from the online measurements was 0.11 µS/cm.

Table 18. Lab results of the SAC effluent on condensate water for the period 03/09 till 27/09.

	Cond.	NH ₃	SiO ₂	PO ₄	Cl	SO ₄	NO ₂	NO ₃	Br	F
	µS/cm	mg/l	µg/l	µg/l	µg/l	mg/l	mg/l	mg/l	mg/l	mg/l
σ	0.21	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Average	1.10	< 0.05	<10.0	<10.0	<100.0	<0.1	<0.1	<0.1	<0.1	<0.1

	Ca	Cr	Cu	Fe	K	Mg	Na*	Ni	Zn	TOC
	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	ppb
σ	0.0	0.0	0.0	6.37	0.0	3.28	0.0	0.0	0.0	16.58
Average	<10	<0.8	<1.0	7.65	<10.0	3.88	<10	<1.0	<1.0	74.79

*The sodium levels were sometimes elevated, but most probably these values were from samples taken just prior to a regeneration as the values decreased in the following samples. However, at those moments in time, the feed water showed also elevated values in Na concentration.

The TOC concentration of the SAC effluent was similar to the feed water at the time of testing, indication that the SAC column did not remove TOC components. The SAC column was able to remove all the ammonia to below the detection limit. The components which were not retained by the SAC were iron and magnesium

and only half of the iron was removed by the MB, while magnesium was totally not removed. The results for the MB effluent are given in Table 19.

Table 19. Lab results of the MB effluent on condensate water for the period 03/09 till 27/09.

	Cond.	NH ₃	SiO ₂	PO ₄	Cl	SO ₄	NO ₂	NO ₃	Br	F
	μS/cm	mg/l	μg/l	μg/l	μg/l	mg/l	mg/l	mg/l	mg/l	mg/l
σ	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Average	-	< 0.05	<10.0	<10.0	<100.0	<0.1	<0.1	<0.1	<0.1	<0.1

	Ca	Cr	Cu	Fe	K	Mg	Na*	Ni	Zn	TOC
	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	ppb
σ	0.0	0.0	0.0	2.43	0.0	1.03	0.0	0.0	0.0	3.36
Average	<10	<0.8	<1.0	3.31	<10.0	3.07	<10	<1.0	<1.0	39.06

*The sodium levels were sometimes elevated, values up to 66 μg/l were measured.

In the MB effluent, the TOC concentration was on average half of the incoming feed water. The removed TOC components were removed by the anion exchange resin in the MB column. Parameters that are too high in concentration are iron and sometimes sodium. Whenever the sodium level was elevated, this was the effect of the incoming water quality, as at those moments the feed sodium concentration went up to 116 μg/l while on average the concentration was below detection limits. The reason for these sudden peaks in sodium concentration should be investigated in order to have a stable operation of the SAC-MB treatment.

Electrodialysis reversal

The EDR was attempted to be operated on condensate in the first part of September, however, it exhibited severe problems with clogging. This was rather surprising, considering the overall excellent quality measurements from the laboratory. After disassembly and cleaning of the feed channel spacers, the clogging was found out to be caused by fibrous clogging (Figure 32), mainly at the inlet of the channels (Figure 33).

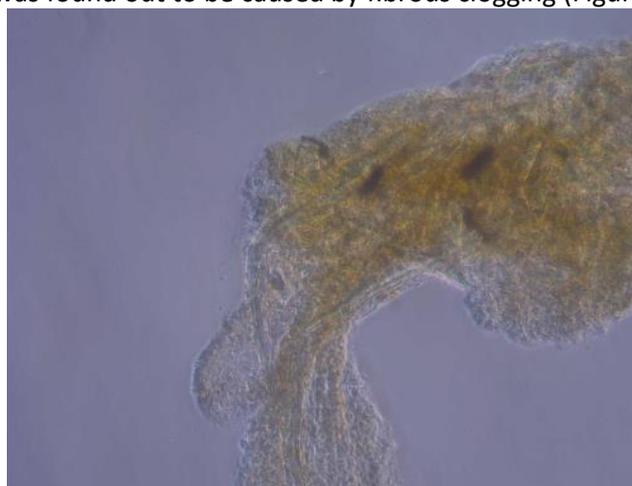


Figure 32. The channel clogging on the EDR was of fibrous nature

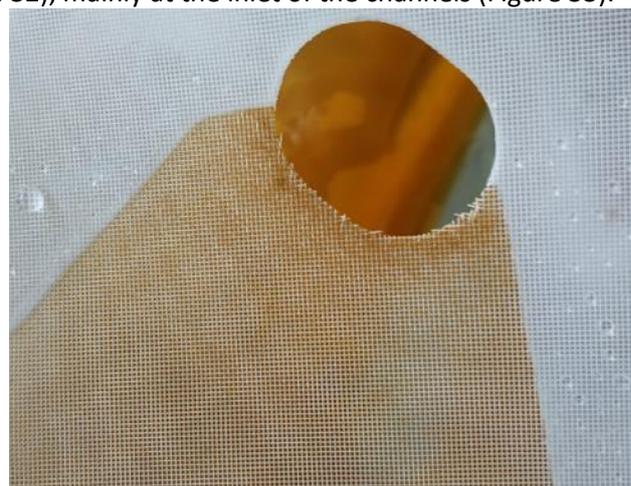


Figure 33. The clogging was mainly observed in the inlets of the spacer channels

A sample of the fouling was sent to the laboratory of BASF for analysis of ions and metals as well as to flow cytometry for investigation of microbial activity. The analysis revealed that the fouling was mainly cellulose

and had no microbial fingerprint. Therefore, the fibers are probably coming from the condensate filtration of BASF, which is done with cellulose filters. Further optimization of the condensate filtration at BASF is advised. To prevent clogging of the EDR, the inline cartridge filters of 60 µm were replaced by 20 µm ones, which resolved the problem.

Reliable measurements with the EDR were taken in the period of 1st to 4th of October, when the inflow was spiked condensate. The EDR was operated in continuous mode, i.e. the diluate was flown only once through the EDR stack and only the concentrate side was recirculated. There was still a minor leak between the two compartments due to a small rupture in one of the membranes, which reduced the maximum concentrate conductivity that could be obtained. To solve this problem, a slight overpressure of 0.05 bar was kept on the diluate side to keep a good diluate quality and the target for maximum concentrate conductivity was set to 40 µS/cm. The resulting operation of the EDR in the spiking period can be seen in Figure 34:

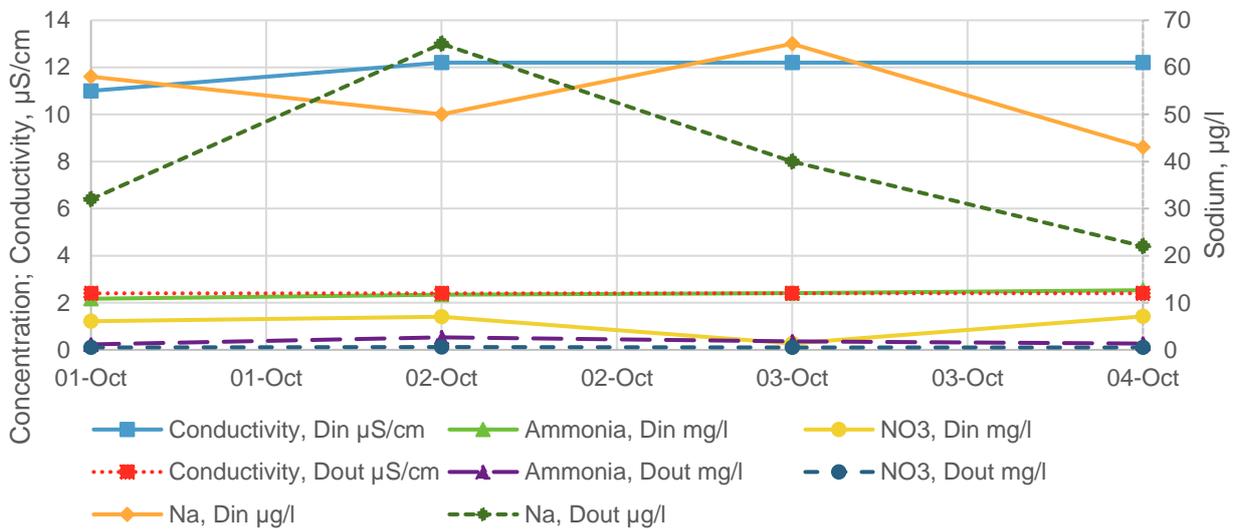


Figure 34. EDR performance during the spiking experiments with condensate

The average pH of the diluate in was 8.9 (±0.04). Since the system was operated in single pass mode, the diluate in (D_{in}) tank should have the same concentrations as the condensate feed. This holds true for all the components except for NO₃, which is below detection limits for the feed water but can be found in small concentrations (around 1.1 mg/l) inside the EDR buffer tank from previous cleaning in place with nitric acid (HNO₃). The NO₃ was rather well rejected, since in most of the measurements in the diluate out it was below the detection limit of 0.1 mg/l, with an average rejection of more than 91%. The ammonia in the condensate feed was around 2.4 mg/l in the diluate in and was on average 1.03 mg/l in the diluate out (57% rejection). The average sodium in the inlet diluate was 54 µg/l and in the outlet it was 39 µg/l, i.e. a rejection of 28%. Finally, the conductivity was 11.9 and 2.4 µS/cm in the diluate inlet and outlet, respectively, i.e. a rejection of 79%. Grab samples of TOC showed a statistically insignificant rejection for TOC (21%) with 121±21 µg/l in the diluate in, compared to 95±26 µg/l for the diluate outlet.

The silica was not rejected by EDR, which is expected because it is not charged. However, the MB as a mixture of strong acid and strong basic resin is known to be able to remove silica. At the interface of the resins the pH changes because the cations are replaced with H⁺ ions and the anions are replaced with OH⁻ ions, which can affect the ionization behavior of silica or to simply reduce the solubility to the point where silica is adsorbed on the surface of the resins. On the other hand, in the EDR, the charged ions are removed due to

interaction with the externally applied electric field, but there is no pH change. While the solubility of silica is affected by pH, with a minimum at pH 7, this effect is not so strong and the minimum solubility is at 100 mg/l at pH 7, while the mixed beds can remove silica to much lower concentrations of around 50 µg/l (Table 4). Therefore, it is more likely that the pH affects the ionizability and polymerization behavior of silica, which is later attached to the ion exchange resins. An interesting source of information of the water treatment chemistry of silica by P. Meyers can reveal more information on the subject [9].

Conversely in the EDR, the ions are simply transported through the membrane due to difference in electric potential and the ions are not exchanged for H⁺ or OH⁻ and the pH is not affected by the ion transport.

The average water recovery was 90.2%. Considering 140 l/h and 165 l/h recirculation flow rate for the diluate and the concentrate and pressure of 0.7 bar of both channels, the hydraulic power needed to operate the stack is 6 W, i.e. a specific pumping energy of 0.050 kWh/m³ of produced water. The stack was operated with 22 cell pairs at 43 volts, however, the current was too low to be able to measure it (limit of 0.01 A). Considering the worst-case scenario of 0.01 A, the desalination power would be 0.43 W or a specific desalination energy demand of 0.003 kWh/m³ of desalinated water. The total specific electrical energy for pumping and desalination for one cubic meter of water is 0.054 kWh/m³.

d) Economic analysis

For each technology the cost for maintenance was assumed to be 3% of the total investment per year. Excluded costs are engineering costs, hours for building, raw water, discharge, permits and inspection, risk and profits, sampling and analyses, man hours for operation and redundancy. The maintenance is considered as 3% of the initial investment per year.

The economic analysis was done, based on general (DACE) cost engineering indicators. For the Biesbosch case the cost of the MB is omitted from the IX calculation, because the other techniques require MB as well to reach boiler feed water quality. Scaling-up the RO and IEX can be done with more confidence compared to the other more novel techniques. The usage of chemicals can differ significantly on full-scale.

This economic analysis should be considered as a techno-economic feasibility study and not as prices for a full-scale installation.

The Biesbosch case

The economic analysis for the Biesbosch case is calculated for a capacity of 900 m³/h - Table 20.

Table 20. Capital and operational expenses per year for the Biesbosch case

	CapEx (M€)	OpEx /year (M€)
RO	2.008	1.077
EDR	4.323	0.646
MD	23.007	4.632
IEX (without MB)	2.475	1.893

The details of the economic analysis for the Biesbosch case can be seen in Appendix A.3.

The four largest operational expenses for RO are the electrical energy, dosing of anti-scalants, cartridge filter replacement and module replacement.

For the EDR, one of the larger operational expenses are the maintenance costs as well as membrane and electrode replacement costs and cartridge filters. It should be noted that a more adequate pretreatment of the water such as coagulation/flocculation and sand filtration is recommended. HCl is considered for CIP costs and the NH₄Cl is considered as biocide. The membranes, electrodes and stack accessories and civil (building to house the technology) are the main expenses.

For the case of MD, the thermal load that was applied in the containers was too low and consequently, the flux was also too low, the economic analysis was performed with data provided from the MD manufacturer – Aquastill. The membrane module considered in the economic analysis was 14.4 m². The flux is expected to be 6.7 l/(m².h) at inlet temperatures 80 and 25 °C for the hot and cold channels respectively at 2.7 m³/h recirculation flow rate. The price of this module is 2500 €, but is assumed to be reduced to 2000 € if ordered in bulk. The membrane lifetime is assumed to be 5 years. It should be noted that the MD capital expense for treating Biesbosch water is considerably higher than the other technologies due to a combination of low flux and expensive modules. The operation expense of MD is also considerably higher than the other technologies, but this is mainly because of maintenance which is based on 3 % of CapEx per year and membrane replacement expenses.

Regarding the case of IEX, without the consideration of MB, the major capital expense for operation are the chemicals for regeneration. In terms of capital expenses, the resin and the vessels are the largest expense.

A summary for the capital and operational expenses for these technologies can be seen by summing the CapEx with the OpEx for the years of operation of the system:

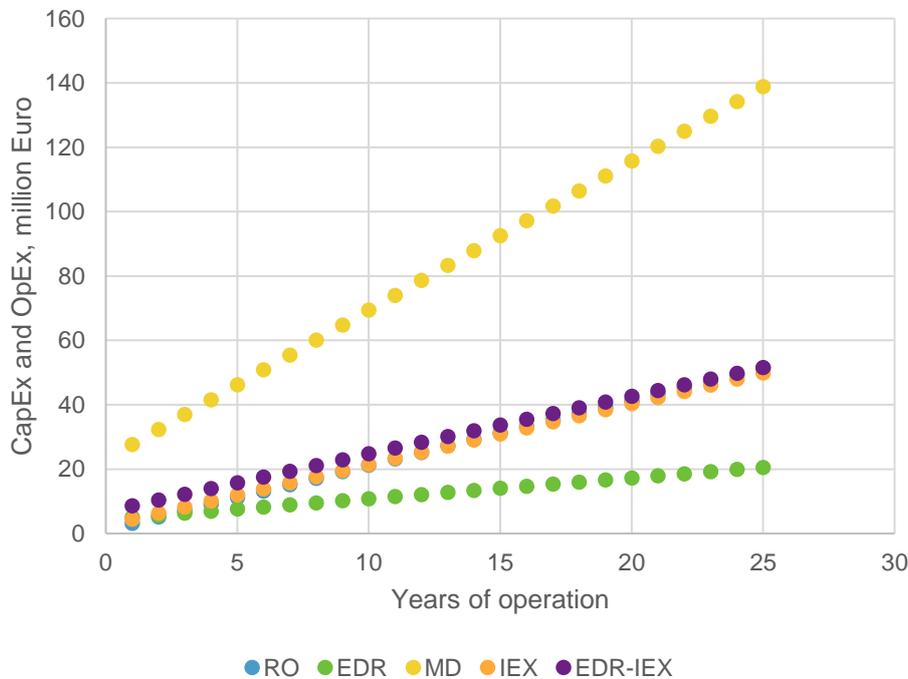


Figure 35. Summation of the CapEx and OpEx as a function of years of operation for the Biesbosch case. The calculation does not include depreciation, inflation and consideration for return of investments.

Most noticeably, the membrane distillation is the most expensive technology due to high initial investment for membranes as well as OpEx for membrane replacement. It is not surprising to see this, as the MD

literature is mainly oriented to treating brine streams where other technologies fail due to osmotic pressure. On the other hand, the EDR has very low OpEx and therefore is the cheapest technology in the long run. However, it should be noted that while RO, MD and IEX have comparable water quality in terms of conductivity and TOC, the EDR can only reduce the conductivity by 30-50 percent for a single pass. Therefore, a case where EDR is coupled with IEX was simulated by summing up the CapEx and OpEx of the two technologies, but assuming half of the use for acid and base for regeneration of the IEX. This case performs comparably to RO and IEX, but the added complexity does not justify its application.

The RO and IEX perform very similar in terms of cost. Both technologies need a mixed bed to achieve boiler feed water quality, however the conductivity of RO permeate is slightly higher at 6.7-12.8 $\mu\text{S}/\text{cm}$, compared to 1-3.2 $\mu\text{S}/\text{cm}$ for the IEX and therefore the MB load of the RO will be higher. It should be noted that the RO also has lower recovery at 75% compared to 95% for the IEX.

However, the RO has the significant advantage of much higher TOC removal, especially in the fall period. During the autumn period the IEX effluent can exceed TOC of over 250 $\mu\text{g}/\text{l}$ (the specified boiler feed water limit of BASF), the RO produces water with TOC of less than 50 $\mu\text{g}/\text{l}$ for the same period. Moreover, the RO uses much less acid and base, needed only for cleaning in place. Therefore, even with higher cost of CapEx and OpEx at 20 years of service, the RO is advised for implementation.

The F200 case

The economic analysis was performed with the technologies scaled-up to 150 m^3/h , the capacity of the F200 process condensate stream.

Table 21. Capital and operational expenses per year for the F200 case

	CapEx (M€)	OpEx /year (M€)
RO	0.688	0.097
MS	4.325	0.692

The detailed economic analysis for the F200 case can be seen in Appendix A.3.

Regarding the MS stripping, similarly to the Biesbosch case, the economic analysis was performed using a 14.4 module instead of the 7.2 m^2 module used in the experiment. Also, a price per module of 2000 euro was used, slightly lower than the offer of 2500 euro, assuming a reduction in the price when ordered in bulk.

A summary for the capital and operational expenses for these technologies can be seen by summing the CapEx with the OpEx for the years of operation of the system:

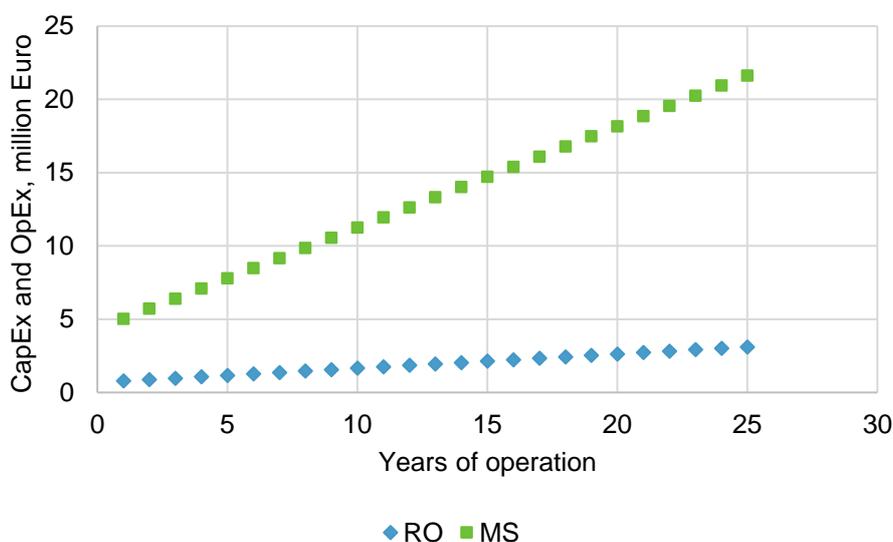


Figure 36. Summation of the CapEx and OpEx as a function of years of operation for the F200 stream. The calculation does not include depreciation, inflation and consideration for return of investments.

Unfortunately, the membrane stripping has a very high capital and operational cost and is not recommended for implementation at this stage.

The RO was producing permeate with boiler feed water quality, but it should be stressed that a better pretreatment might be needed because of the feed spacer fouling observed in the experiments.

The general condensate stream

The economic analysis was performed for technologies scaled-up for 600 m³/h, the capacity of the GDW stream **Table 22**.

Table 22. Capital and operational expenses per year for the GDW case

	CapEx (M€)	OpEx /year (M€)
RO	1.317	0.375
EDR	2.589	0.358
SAC (SAC-MB)	0.584	0.168
MB (SAC-MB)	0.655	0.151
MB (Standalone)	0.758	0.268

The detailed economic analysis for the GDW case can be seen in Appendix A.3.

While antiscalants are not needed to operate the RO on the condensate stream, some HCl is still considered for cleaning in place in case of iron fouling as well as NaOH for cleaning of organic fouling and possibly cellulose fibers that are present in the stream as seen in the EDR application.

For the EDR, the major operational expense is replacement the electrodes and membranes. It should be noted that the EDR has quite large capital expense.

The sum of CapEx and OpEx was compared for all technologies as a function of service time - **Figure 37**.

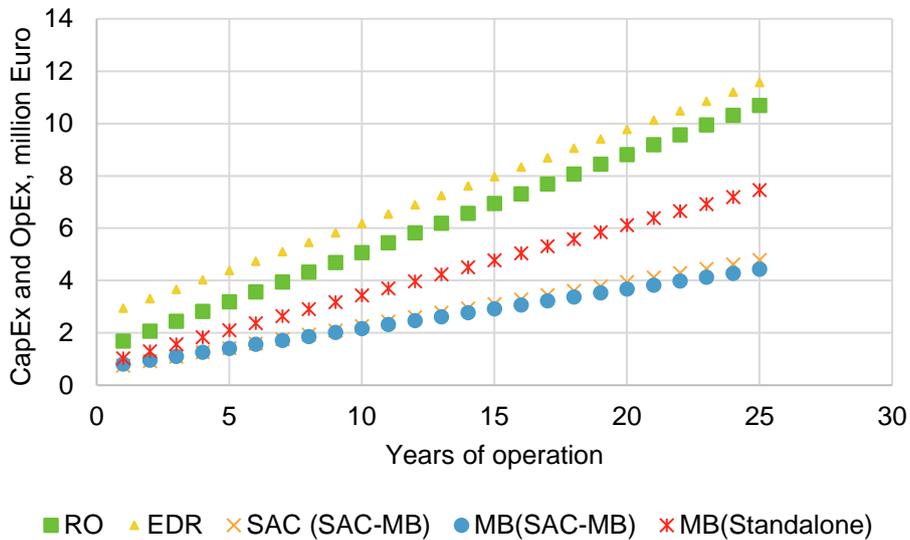


Figure 37. Summation of CapEx and OpEx as a function of years of operation for the condensate stream case (GDW). The calculation does not include depreciation, inflation and consideration for return of investments.

The EDR has the highest cost for a 20 years operation period, as well as the lowest quality of the effluent and is therefore not recommended for implementation on this stream. The RO and the SAC have a comparable performance in terms of permeate quality. The RO has an average TOC of 40, the standalone MB had a TOC of 36 and the SAC-MB configuration had a TOC of 39 ppb.

The normal conductivity of the RO for this period was 10.7 $\mu\text{S}/\text{cm}$, however most of it was ammonia which is added for corrosion protection. The degassed cation conductivity most of the time indicated that the RO was able to bring the water to boiler feed water specifications, but during a certain period the permeate quality had degassed cation conductivity higher than 0.5 $\mu\text{S}/\text{cm}$ due to variation in the feed composition.

The standalone mixed bed had good quality for TOC of 36 $\mu\text{g}/\text{l}$ on the average, but the degassed cation conductivity most of the time was above 0.2 $\mu\text{S}/\text{cm}$. On the other hand the SAC-MB configuration had a low TOC of 36 ppb and degassed cation conductivity of less than 0.11 $\mu\text{S}/\text{cm}$ for the tested period. Moreover, at 20 years of service, the SAC-MB configuration has a comparable sum of CapEx and OpEx to the standalone mixed bed which has inferior water quality. Therefore, the SAC-MB technology seems to be best suited for full-scale application on the GDW case.

Conclusion

The Biesbosch case

A summary of the performance of the different technologies can be seen in Table 23:

Table 23. Summary of the technologies tested on Biesbosch water

	SEC (kWh/m ³)	Recovery (%)	Conductivity (µS/cm)	TOC (µg/l)	CapEx (M€)	OpEx (M€/y)
Ion exchange	0.02	96	2.1	82(after MB)	2.01	1.08
RO	0.23	75	8.2	46	4.32	0.65
MD	0.68	25	4.2	87	23.01	4.63
EDR	0.09	95	384	2388	2.48	1.89

Based on the above results and the economic analyses done in this work, the most promising technology for the treatment of the Biesbosch surface water is IEX or RO. Due to the high initial investment costs for both EDR and MD, these technologies are not likely to be implemented. The IEX treatment can provide a good boiler feed water quality, but uses a lot of chemicals during the production process, mainly due to the need for regeneration chemicals. Also, the IEX even after a mixed bed failed to meet the TOC limit of 250 µg/l effluent.

In comparison, the single pass RO does not meet the boiler feed water quality immediately, but uses less environmentally sensitive chemical components. A RO followed by a MB will have the excellent TOC rejection of the RO combined with the excellent ion-polishing performance of the MB and therefore this technology is recommended for full-scale application.

F200 process condensate

Table 24. Summary of the technologies tested on F200 process condensate

	SEC (kWh/m ³)	Recovery (%)	Conductivity (µS/cm)	TOC (µg/l)	CapEx (M€)	OpEx (M€/y)
RO	0.28	85	11.2*	103	0.69	0.10
MS	0.16	100	-	-	4.33	0.69

* (degassed cation conductivity 0.18)

The membrane stripping was performing satisfactory for ammonia recovery but is not economically feasible for implementation due to high investment cost, combined with low ammonia concentration in the feed stream, which is not favorable for the process.

The F200 process condensate was treated very well in terms of product quality by RO but the technology exhibited problems with feed spacer fouling. The fouling was probably caused by iron induced biofouling, but this needs to be further confirmed. Besides the problems with the feed spacer fouling, the permeate quality was very good and achieved boiler feed water specifications in terms of degassed cation conductivity and TOC rejection. It should be noted that even though the degassed cation conductivity was always below 0.2 µS/cm, the RO permeate contained a lot of ammonia and will load a polishing technology such as a mixed bed, in case polishing is needed.

General condensate stream

Table 25. Summary of the technologies tested on general condensate stream

	SEC (kWh/m ³)	Recovery (%)	Conductivity (µS/cm)	TOC (µg/l)	CapEx (M€)	OpEx (M€/y)
RO	0.21	85	10.7 (0.22 degassed cation conductivity)	40.9	1.32	0.38
MB			<0.4 degassed cation conductivity	36	2.59	0.36
SAC-MB			0.11 degassed cation conductivity	39	0.58	0.17
EDR	0.05	90.2	2.4	95	0.66	0.15

The EDR removed most of the ammonia and had very low specific energy consumption to treat the stream. Initially, channel spacer clogging was observed, but this was solved by employing tighter cartridge filters as pretreatment. The technology could work very well as a pretreatment for mixed bed, minimizing the regeneration input of chemicals by removing the ammonia which otherwise loads the cation exchanger resins. However, the EDR requires rather large capital investment due to expensive membranes and modules.

The quality of the RO permeate when aimed at reuse as boiler feed water was satisfactory, but it should be noted that in some periods the degassed cation conductivity exceeded the limit value, probably due to specific composition of the condensate feed. Also, the RO is less economically feasible for application on condensate streams compared to resin technologies. It should also be considered that the RO stream contains a lot of ammonia. On one hand this is positive, since if the stream is clean enough for reuse, the ammonia does not need to be injected additionally (for corrosion control), however if the water needs further polishing, the ammonia will load the polishing technology – e.g. a mixed bed.

The standalone mixed bed performed well in terms of TOC rejection, but did not meet the degassed cation conductivity limit of 0.2 µS/cm. When combined with SAC in front of the MB, the quality was excellent both in terms of conductivity and TOC. Considering that the technology also has very low combined cost, it can be recommended for implementation on full-scale.

5. Acknowledgments

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List of abbreviations

IEX	ion exchange
EDR	electrodialysis reversal
RO	reverse osmosis
CIP	cleaned-in-place
TOC	total organic carbon
CEM	cation exchange membrane
AEM	anion exchange membrane
NSP	normalized salt passage
MTC	mass transfer coefficient

Appendices

A.1 Composition of the Biesbosch period RO feed water and RO permeate

Table 26. Laboratory analysis of the Biesbosch water with MCA and 54% potable water without SBS neutralization 24/07/2018 to 27/07/2018

	pH	Temp.	Cond.	NPOC	NH ₃	SiO ₂	PO ₄	Cl	SO ₄	NO ₂	NO ₃	Br
		°C	µS/cm	mg/l	mg/l	µg/l	µg/l	µg/l	mg/l	mg/l	mg/l	mg/l
Average	8.1	16.5	473.7	1.36	0.07	4872	27	38425	43.6	0.1	7.9	0.1
σ	0.0	0.6	2.6	0.07	0.01	289	3	884	1.8	0.0	0.6	0.0
	F	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC	
	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	
Average	0.2	55831	0.80	1.00	40.2	4689	6569	30990	1.2	6.6	1477	
σ	0.0	2952	0.00	0.00	27.3	200	338	1208	0.0	0.3	76	

Table 27. Composition of the RO permeate on Biesbosch water with 54% potable water without SBS neutralization 24/07/2018 - 27/07/2018

	Cond.	NH ₃	SiO ₂	PO ₄	Cl	SO ₄	NO ₂	NO ₃	Bromide	Fluoride
	(µS/cm)	mg/L	µg/L	µg/L	µg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Average	8.2	0.1	76.8	10.0	700.0	0.1	0.1	0.7	0.1	0.1
σ	0.7	0.0	12.3	0.0	70.7	0.0	0.0	0.1	0.0	0.0
	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	ppb
Average	133.0	0.8	1.0	2.3	197.0	26.0	1142.0	1.0	1.0	4.6
σ	41.4	0.0	0.0	2.2	21.0	10.8	54.8	0.0	0.0	1.1

Table 28. Laboratory analysis of the Biesbosch water with MCA without SBS neutralization 17/10/2018 to 08/11/2018

	pH	Temp.	Cond.	NPOC	NH ₃	SiO ₂	PO ₄	Cl	SO ₄	NO ₂	NO ₃	Br
		°C	µS/cm	mg/l	mg/l	µg/l	µg/l	µg/l	mg/l	mg/l	mg/l	mg/l
σ	0.1	2.1	43	0.3	0.1	316	7.6	4166	3.1	0.0	0.8	0.0
Average	8.3	8.5	566	1.7	0.2	4134	17.2	63046	56.3	0.1	7.4	0.1
	F	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC	
	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	
σ	0.1	14308	0.2	0.1	9.3	1748	1794	11224	0.4	1.0	421	
Average	0.3	60269	0.9	1.1	27.5	6945	8111	46305	2.2	8.6	2418	

Table 29. Laboratory analysis of the RO permeate on Biesbosch water with MCA without SBS neutralization
17/10/2018 to 08/11/2018

	Cond.	NH₃	SiO₂	PO₄	Cl	SO₄	NO₂	NO₃	Br	F
	(μ S/cm)	mg/L	μ g/L	μ g/L	μ g/L	mg/L	mg/L	mg/L	mg/L	mg/L
σ	1.7	0.1	10.1	0.0	180.3	0.1	0.0	0.3	0.0	0.0
Average	6.7	0.2	34.9	10.0	750.0	0.2	0.1	0.5	0.1	0.1
	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC
	μ g/L	μ g/L	μ g/L	μ g/L	μ g/L	μ g/L	μ g/L	μ g/L	μ g/L	ppb
σ	43718.1	0.0	0.5	6.3	5524.7	6246.0	33682.5	1.2	4.3	40.8
Average	21636.6	0.8	1.1	2.8	2850.7	3073.2	17462.1	1.3	2.2	45.7

A.2 Composition of the F200 for the November period.

	pH	Temp	Cond	NPOC	NH ₃	SiO ₂	PO ₄	Cl	SO ₄	NO ₂	NO ₃	Br
				mg/L	mg/L	µg/L	µg/L	µg/L	mg/L	mg/L	mg/L	mg/L
σ	0.0	1.6	4.0	0.0	0.5	1.8	24.4	0.0	0.0	0.0	0.0	0.0
Average	8.4	26.3	53.5	0.4	8.9	15.2	22.2	100.0	0.1	0.1	0.1	0.1
	F	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Zn	TOC	
	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	ppb	
	0.0	3.8	0.0	0.0	6.4	10.6	2.9	22.4	0.0	0.0	181.4	
σ	0.1	14.6	0.8	1.0	52.9	87.6	12.6	70.2	1.0	1.0	482.4	
Average												

A.3 Economic analysis

The Biesbosch case

Table 30. Economic analysis of the RO for the Biesbosch case

OpEx	Amount	Unit	Price	Unit	Costs/year
Energy	6,897,979	kWh/year	€ 0.08	/kWh	€ 551,838.30
HCl					€ 5,144.30
Anti-scalant	34,333	kg/year	€ 5.00	/kg	€ 171,666.00
NaOH					€ 7,716.44
Maintenance					€ 60,243.00
Cartridge filters					€ 156,000.00
Module replacement					€ 124,875.00
Total					€ 1,077,483.04

CapEx	Amount	Unit	Price	Unit	Costs
RO modules					€ 499,500.00
Pressure vessels	222	-	€ 600.00	/PV	€ 133,200.00
Pumps					€ 250,000.00
Chemical storage and dosing	3	-	€ 25,000.00	/unit	€ 75,000.00
CIP tank & pump	2		€ 25,000.00		€ 50,000.00
Buffer					€ 107,200.00
Piping and valves					€ 174,200.00
Electrics and instrumentation					€ 268,000.00
Civil					€ 201,000.00
Process automation					€ 250,000.00
Total					€ 2,008,100.00

Table 31. Economic analysis for EDR for the Biesbosch case

Cartridge filters	Amount	Unit	Price	Unit	Costs/year
Energy	796,699	kWh/year	€ 0.08	/kWh	€ 63,735.92
HCl					€ 2,521.84
NH ₄ Cl					€ 40,728.79
Maintenance					€ 129,693.00
Membrane and electrode replacement					€ 254,157.31
Cartridge filters					€ 156,000.00
Total					€ 646,836.85

CapEx	Amount	Unit	Price	Unit	Costs
ED membranes and electrodes	53.5	-	€ 41,459.82	/stack	€ 2,218,100.14
Stack accessoires					€ 400,000.00

Pumps				€ 150,000.00
Chemical storage and dosing	4	-	€ 25,000.00 /unit	€ 100,000.00
CIP tank & pump	2		€ 25,000.00	€ 50,000.00
Buffers				€ 175,000.00
Piping and valves				€ 230,000.00
Instrumentation & electrics				€ 250,000.00
Civil				€ 500,000.00
Process automation				€ 250,000.00
Total				€ 4,323,100.14

Table 32. Economic analysis of MD for the Biesbosch case

OpEx	Amount	Unit	Price	Unit	Costs/year
Electric energy	2,440,286	kWh/year	€ 0.08	/kWh	€ 195,223
HCl					€ 10,000
NaOH					€ 10,000
Maintenance					€ 690,214
Membrane replacement					€ 3,571,429
Cartridge filters					€ 156,000.00
Total					€ 4,632,866
Heating (thermal energy)		MWh/y			2732035
Cooling (thermal energy)		MWh/y			2440286

CapEx	Amount	Unit	Price	Unit	Costs
MD membranes	8929	-	€ 2,000.00	/module	€ 17,857,143
Skid accessories					€ 900,000
Pumps					€ 350,000
Heating and cooling equipment					€ 2,000,000
Chemical storage and dosing	2	-	€ 25,000.00	/unit	€ 50,000
CIP tank & pump	2		€ 25,000.00	/unit	€ 50,000
Buffer					€ 150,000
Piping and valves					€ 250,000
Instrumentation & electrics					€ 400,000
Civil					€ 600,000
Process automation					€ 400,000
Total					€ 23,007,143

Table 33. Economic analysis for ion exchange for the Biesbosch case

OpEx	Amount	Unit	Price	Unit	Costs/year
Energy	1,148,727	kWh/year	€ 0.08	/kWh	€ 91,898.17
HCl					€ 405,328.91
NaOH					€ 1,149,077.41
Maintenance					€ 74,271.94



Resin replacement	€ 172,614.29
Total	€ 1,893,190.71

CapEx	Amount	Unit	Price	Unit	Costs
Resins					€ 825,331.25
IX vessels	10	-	€ 40,000.00	/vessel	€ 400,000.00
Pumps					€ 250,000.00
Chemical storage and dosing	2	-	€ 80,000.00	/unit	€ 160,000.00
Degassers	5		€ 10,000.00		€ 50,000.00
Buffer					€ 107,200.00
Piping and valves					€ 64,200.00
Electrics and instrumentation					€ 168,000.00
Civil					€ 201,000.00
Process automation					€ 250,000.00
Total					€ 2,475,731.25

The F200 case

Table 34. Economic analysis for RO on the F200 case

OpEx	Amount	Unit	Price	Unit	Costs/year
Energy	430,603	kWh/year	€ 0.08	/kWh	€ 34,448.23
HCl					€ 602.49
Anti-scalant	0	kg/year	€ 5.00	/kg	€ -
NaOH					€ 903.73
Maintenance					€ 20,643.00
Cartridge filters					€ 26,000.00
Module replacement					€ 14,625.00
Total					€ 97,222.44

CapEx	Amount	Unit	Price	Unit	Costs
RO modules					€ 58,500.00
Pressure vessels	26	-	€ 600.00	/PV	€ 15,600.00
Pumps					€ 60,000.00
Chemical storage and dosing	3	-	€ 10,000.00	/unit	€ 30,000.00
CIP tank & pump	2		€ 10,000.00		€ 20,000.00
Buffer					€ 60,000.00
Piping and valves					€ 75,000.00
Electrics and instrumentation					€ 168,000.00
Civil					€ 101,000.00
Process automation					€ 100,000.00
Total					€ 688,100.00

Table 35. Economic analysis of the membrane stripping for the F200 case

OpEx	Amount	Unit	Price	Unit	Costs/year
Electric energy	207,612	kWh/year	€ 0.08	/kWh	€ 16,609
HCl					€ 10,000
NaOH					€ 10,000
Maintenance					€ 129,750
Membrane replacement					€ 500,000
Cartridge filters					€ 26,000.00
Total					€ 692,359

CapEx	Amount	Unit	Price	Unit	Costs
MD membranes	1250	-	€ 2,000.00	/module	€ 2,500,000
Skid accessories					€ 300,000
Pumps					€ 250,000
Heating and cooling equipment					€ 500,000
Chemical storage and dosing	2	-	€ 25,000.00	/unit	€ 50,000

CIP tank & pump	2	€ 25,000.00 /unit	€ 50,000
Buffers			€ 80,000
Piping and valves			€ 75,000
Instrumentation & electrics			€ 200,000
Civil			€ 200,000
Process automation			€ 120,000
Total			€ 4,325,000

The general condensate stream (GDW)

Table 36. Economic analysis for RO on the general condensate stream

OpEx	Amount	Unit	Price	Unit	Costs/year
Energy	1,967,805	kWh/year	€ 0.08	/kWh	€ 157,424.42
HCl					€ 2,780.70
Anti-scalant	0	kg/year	€ 5.00	/kg	€ 0.00
NaOH					€ 4,171.05
Maintenance					€ 39,510.00
Cartridge filters					€ 104,000.00
Module replacement					€ 67,500.00
Total					€ 375,386.17

CapEx	Amount	Unit	Price	Unit	Costs
RO modules					€ 270,000.00
Pressure vessels	120	-	€ 600.00	/PV	€ 72,000.00
Pumps					€ 150,000.00
Chemical storage and dosing	3	-	€ 25,000.00	/unit	€ 75,000.00
CIP tank & pump	2		€ 25,000.00		€ 50,000.00
Buffer					€ 80,000.00
Piping and valves					€ 120,000.00
Electrics and instrumentation					€ 200,000.00
Civil					€ 150,000.00
Process automation					€ 150,000.00
Total					€ 1,317,000.00

Table 37. Economic analysis for the EDR on the general condensate case

OpEx	Amount	Unit	Price	Unit	Costs/year
Energy	331,128	kWh/year	€ 0.08	/kWh	€ 26,490.24
HCl					€ 1,272.70
NH ₄ Cl					€ 20,554.71
Maintenance					€ 77,682.45
Membrane and electrode replacement					€ 128,266.31
Cartridge filters					€ 104,000.00
Total					€ 358,266.41

CapEx	Amount	Unit	Price	Unit	Costs
ED membranes and electrodes	27	-	€ 41,459.82	/stack	€ 1,119,415.03
Stack accessories					€ 300,000.00
Pumps					€ 100,000.00
Chemical storage and dosing	4	-	€ 25,000.00	/unit	€ 100,000.00
CIP tank & pump	2		€ 25,000.00		€ 50,000.00

Buffers	€ 120,000.00
Piping and valves	€ 150,000.00
Instrumentation & electrics	€ 150,000.00
Civil	€ 300,000.00
Process automation	€ 200,000.00
Total	€ 2,589,415.03

Table 38. Economic analysis for the SAC on the general condensate stream (from SAC-MB configuration) for the GDW case

OpEx	Amount	Unit	Price	Unit	Costs/year
Energy	664,219	kWh/year	€ 0.08	/kWh	€ 53,137.52
HCl					€ 89,619.67
NaOH					€ 0.00
Maintenance					€ 17,538.30
Resin replacement					€ 7,801.43
Total					€ 168,096.91

CapEx	Amount	Unit	Price	Unit	Costs
Resins					€ 54,610.00
IX vessels	4	-	€ 40,000.00	/vessel	€ 160,000.00
Pumps					€ 80,000.00
Chemical storage and dosing	1	-	€ 40,000.00	/unit	€ 40,000.00
Piping and valves					€ 60,000.00
Electrics and instrumentation					€ 40,000.00
Civil					€ 100,000.00
Process automation					€ 50,000.00
Total					€ 584,610.00

Table 39. Economic analysis for the mixed bed (from SAC-MB configuration) for the GDW case

OpEx	Amount	Unit	Price	Unit	Costs/year
Energy	727,543	kWh/year	€ 0.08	/kWh	€ 58,203.42
HCl					€ 9,215.63
NaOH					€ 44,405.47
Maintenance					€ 19,649.79
Resin replacement					€ 19,348.75
Total					€ 150,823.05

CapEx	Amount	Unit	Price	Unit	Costs
Resins					€ 84,993.00
IX vessels	4	-	€ 50,000.00	/vessel	€ 200,000.00
Pumps					€ 0.00

Chemical storage and dosing	2	-	€ /unit	€ 80,000.00
			40,000.00	
Piping and valves				€ 80,000.00
Electrics and instrumentation				€ 60,000.00
Civil				€ 100,000.00
Process automation				€ 50,000.00
Total				€ 654,993.00

Table 40. Economic analysis for a standalone mixed bed on the GDW case

OpEx	Amount	Unit	Price	Unit	Costs/year
Energy	728,507	kWh/year	€ 0.08	/kWh	€ 58,280.55
HCl					€ 28,414.84
NaOH					€ 136,916.85
Maintenance					€ 22,740.00
Resin replacement					€ 21,760.00
Total					€ 268,112.25

CapEx	Amount	Unit	Price	Unit	Costs
Resins					€ 108,000.00
IX vessels	4	-	€ 50,000.00	/vessel	€ 200,000.00
Pumps					€ 80,000.00
Chemical storage and dosing	2	-	€ 40,000.00	/unit	€ 80,000.00
Piping and valves					€ 80,000.00
Electrics and instrumentation					€ 60,000.00
Civil					€ 100,000.00
Process automation					€ 50,000.00
Total					€ 758,000.00

A.4 Used equations

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

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

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

Where U_{par} is the Dow 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.

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

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

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

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

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

Where NPD is normalized pressure drop [kPa], Q_{feedn} normalized design feed flow of the RO system [$m^3 \cdot h^{-1}$], $Q_{concentraten}$ normalized design concentrate flow [$m^3 \cdot h^{-1}$], 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 Dow membrane values, equal to 1.6 and 0.4, respectively.

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

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

$$T_{cf_OP} = \frac{T_{feed} + 273.15}{T_{ref} + 273.15}$$

$$OP_{feed} = EC_{feed} \times EC_{OP_feed} \times T_{cf_OP}$$

$$OP_{concentrate} = EC_{concentrate} \times EC_{OP_concentrate} \times T_{cf_OP}$$

$$OP_{permeate} = EC_{permeate} \times EC_{permeate} \times T_{cf_OP}$$

Where MTC is the mass transfer coefficient [$\text{m}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$], 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.