

Report Improved

Mobile Research Infrastructure Experiments

Case study at Yara Sluiskil B.V.



2018



The Improved containers at the ureum plant at Yara Sluiskil

Yara Sluiskil B.V. kan op geen enkele wijze aansprakelijk gesteld worden voor de volledigheid en juistheid van de informatie die in dit rapport verstrekt wordt. Ook kunnen geen rechten worden ontleend aan de in dit rapport verstrekte informatie of gegevens. Zonder schriftelijke toestemming van Yara Sluiskil mag niets uit dit rapport gedupliceerd of gedistribueerd worden buiten de in het project betrokken partners.

Case study at Yara Sluiskil B.V.: test period September 2017 - April 2018	
Main authors	Evelyn De Meyer (UGent) Farnoosh Fasaei (HZ)
Correctors	Ewoud Van den Brande (Yara) Paul Van Elslande (Yara) Wilbert van den Broek (Evides industriewater) David Moed (Evides industriewater) Marjolein Vanoppen (UGent) Hans Cappon (HZ)
Others involved	Ann Stevens, Dimitri Overmeire and other lab responsables for the analyses (Yara) Engineers and operators at the nitric acid and ureum department (Yara) Operators at the demineralisation plant (Evides industriewater)

Summary

The IMPROVED (Integrale Mobiele PROceswater Voorziening voor een Economische Delta) project is an initiative in which business and knowledge institutions work closely together. The main objective is to provide sustainable water use in a more economic and efficient way using various water treatment methods, sometimes different methods in succession. For more information, visit website (www.improvedwater.eu). It is one of the projects funded within the Interreg V program Flanders-Netherlands, which is a program developed by a partnership between Flanders and the Netherlands to invest in smart, sustainable and inclusive growth. Improved is one of the flagship projects in the CAPTURE initiative (<https://capture-resources.be>).

Fresh water is of major importance for the chemical industry, as it is used in all kinds of chemical processes. However, the continuous supply becomes more uncertain nowadays, as ground and surface water are overused and/or depleting. The reuse of industrial process water provides a sustainable solution to this challenge. In this research, the potential of new technologies for ultrapure water production from spent condensates and waste streams is investigated, commissioned by the company Yara Sluiskil B.V., in the context of the IMPROVED project. On-site pilot tests were executed from September 2017 until April 2018.

Problem Statement and goal

The treatment of two different process condensate streams of the Yara company, one of the world's largest producers of nitrogen fertilizers and industrial chemicals, were investigated. The main contaminants in the streams are ammonium (NH_4^+) and nitrate (NO_3^-), together with primary alcohols and a small amount of lower organic acids.

The first stream of interest (C1) contains mainly ammonia and nitrate. Currently this stream is fed back to the beginning of the Evides industriewater (wastewater and industrial water treatment company in The Netherlands) water treatment plant (which consists of Ion Exchange columns (IEX)) after neutralization with nitric acid (HNO_3). This current situation is due to the excessive conductivity and/or pH of the condensate stream, which makes it unsuitable for local treatment with the Condensate Polisher Unit (CPU) present at Yara. After the IEX treatment, the water is reused as demineralized water.

The second, a CO_2 condensate stream (C2) contains about 500 ppm TOC (Total Organic Carbon) and is loaded with a high concentration of ammonia together with primary alcohols and methyl diethanolamine (MDEA). Due to the high TOC content, it is not economically feasible to treat this stream with IEX, because the regeneration frequency of the anion resins would be too high. In order to assure that no MDEA is present in the demineralized water, it is discharged via the wastewater. Therefore, other technologies than IEX are investigated for the possible re-use of this condensate stream.

Desalination of the streams was investigated by means of three different techniques: electrodialysis (ED), reverse osmosis (RO) and membrane stripping or distillation (MS/MD, depending on the configuration). ED is an upcoming technique, in which an electrochemical potential difference is used to achieve separation through ion exchange membranes (IEM). RO is a state of the art technique using a hydraulic pressure difference to overcome the osmotic pressure between two solutions and produce a clean permeate. The most recent techniques are MS and MD, where a difference in pH (MS) or in temperature (MD) is applied to

achieve transport through a hydrophobic membrane (either transport of the contaminants or of the pure water, depending on the operational mode).

The main goal for Yara is on the one hand to reuse the treated process condensates in other cycles (e.g. boiler feed water), in order to reduce the use of demineralized water and to decrease the water footprint. On the other hand, the goal is to investigate (especially for the C1 stream) whether the ammonium nitrate that is separated from the condensate can be concentrated and recovered from the process condensate to be reused after treatment, resulting in a much lower environmental impact and cost of discharge. This way, both the polished and the concentrated stream can be re-used to achieve a closed loop in the end.

Outcome

The ultimate selection of the most efficient technology depends highly on what is important for the company and what is the actual aim. So it can change according to the objective, for example in the YARA case for the C1 stream, MD is suggested if the most important aim is the quality of the treated stream, as no additional post treatment step is required to meet the specifications for boiler feed water. Compared to ED and RO, the product quality of the MD permeate was the best, as no ammonia or nitrate went through the membrane. However, this technique is very energy intensive and the flow rate of the product stream is very small. When water efficiency and economic aspects are taken into account, RO is the best alternative to the currently used IEX train.

In general, no decisive difference was observed concerning both the product quality and water efficiency between the RO and ED treatment. It should be mentioned that the specifications for boiler feed water are not met solely with the RO or ED treatment. An extra treatment technology afterwards is therefore necessary, mainly to decrease the concentration of nitrate and to induce a further decrease in conductivity. In addition, the RO concentrate might be sent to the biological waste water treatment plant. This is not possible with the IEX treatment, as the waste water (coming from the regeneration) shows very high pH differences, due to the use of HCl and NaOH.

For the CO₂-condensate stream the same conclusion can be made concerning the economic aspects without focusing on the product quality. During RO treatment MDEA is completely retained by the membrane, while the total of NH₃ and NH₄⁺ is retained for 92-94%, the primary alcohols end up in the permeate due to their neutrality and small molecular size. When the most important factor is the reuse of the ammonia, MS in combination with IEX gives the most promising results. During IEX, ammonia and MDEA can be separated from the primary alcohols as they will be adsorbed on the cation exchange resin. After regeneration, ammonia can be separated from MDEA by MS treatment due to a difference in vapor pressure.

Whenever a certain technology is chosen to be implemented in the future, a more in-depth economic evaluation is necessary to compare the new technology with the current one. In addition, the conclusions stated in this report are based on pilot-scale experiments ran over a limited amount of time. In order to investigate the performance of a new technology, a longer time-frame should be applied for testing stable operation of any specific technology.

Table of contents

List of abbreviations	6
1. Introduction	7
1.1. Problem Statement	7
1.2. Goal.....	8
2. Technologies of interest.....	9
2.1. Electrodialysis	9
2.2. Reverse osmosis	10
2.3. Membrane distillation and stripping.....	11
3. Materials and Method	12
3.1. Electrodialysis	12
3.2. Reverse osmosis	13
3.3. Membrane distillation and membrane stripping	13
3.4. Economic evaluation	13
4. Results and Discussion.....	13
4.1. SR800 stream (C1)	13
4.1.1. Electrodialysis	14
4.1.2. Reverse osmosis	17
4.1.3. Membrane distillation	22
4.1.4. Economic evaluation of the SR800 stream.....	23
4.2. CO ₂ -condensate stream (C2)	26
4.2.1. Electrodialysis	26
4.2.2. Reverse osmosis	30
4.2.3. Membrane stripping.....	34
4.2.4. Economic evaluation of the CO ₂ -condensate stream.....	36
5. Conclusions	39
6. References	40
7. Appendix	41
7.1. Condensate quality Yara Sluiskil B.V. (based on analysis from 2016)	41
7.2. Used equations	41

List of abbreviations

IEX	ion exchange
CPU	condensate polishing unit
MDEA	methyl diethanolamine
EDR	electrodialysis reversal
RO	reverse osmosis
CIP	cleaned-in-place
AIRO	air flush in RO
IEM	ion exchange membranes
TOC	total organic carbon
CEM	cation exchange membrane
AEM	anion exchange membrane
NSP	nominal salt passage
MTC	mass transfer coefficient
SER	specific energy requirement

1. Introduction

The IMPROVED (Integrale Mobiele PROCeswater Voorziening voor een Economische Delta) project is an initiative in which business and knowledge institutions work closely together in order to provide sustainable water use in a more economic and efficient way using various water treatment methods, sometimes different methods in succession. It is one of the projects funded within the Interreg V program Flanders-Netherlands, which is a program developed by a partnership between Flanders and the Netherlands to invest in smart, sustainable and inclusive growth. The European Commission provided a fund that strengthened and promoted innovation and sustainable development in the border region for the building of a plug-and-play mobile water treatment infrastructure.

The project investigates whether it is possible to use other types of water, such as groundwater, surface water, brackish water or waste water instead of drinking water, to produce water of the sufficient quality for industrial processes. By experimentally establishing the desired final quality, one could clearly identify which water sources are possible alternatives, and which purification technology is required. With the knowledge gained during this research project, the water cycle could be closed better to reduce the freshwater demand of the industry.

Fresh water is of major importance for the chemical industry, as it is used in all kinds of chemical processes. However, the continuous supply becomes more uncertain nowadays, as ground and surface water are depleting. The reuse of industrial process water provides a sustainable solution to this challenge. In this research, the potential of new technologies for ultrapure water production from spent condensates and waste streams is investigated, commissioned by the company Yara Sluiskil B.V., in the context of the IMPROVED project. Pilot tests are executed from September 2017 until April 2018.

1.1. Problem Statement

In this work, the treatment of two different process condensate streams of the Yara company, one of the world largest producer of nitrogen fertilizers and industrial chemicals, were investigated. The main contaminants in the streams are ammonium (NH_4^+) and nitrate (NO_3^-), together with primary alcohols and a small amount of lower organic acids.

The first stream of interest (from now on referred to as C1), coming from the ammonium nitrate production plant SR800, contains mainly ammonia and nitrate. Currently this stream is fed back to the beginning of the *Evides industriewater* (wastewater and industrial water treatment company in The Netherlands) water treatment plant (which consists of Ion Exchange columns (IEX)) after neutralization with nitric acid (HNO_3). This current situation is due to the excessive conductivity and/or pH of the condensate stream (mainly due to high amounts of nitrate), which makes it unsuitable for local treatment with the Condensate Polisher Unit (CPU, where impurities are being removed) present at Yara. After the IEX treatment, the water is reused as demineralized water.

The second, a CO_2 condensate stream (from now on referred to as C2), coming from the urea producing plant, contains about 500 ppm TOC and is loaded with a high concentration of ammonia together with primary alcohols and methyl diethanolamine (MDEA). Due to the high TOC content, it

is not economically feasible to treat this stream with IEX, because the regeneration frequency of the anion resins would be too high. Currently, this condensate cannot be re-used, because acidic decomposition products could be produced from the alcohols in the steam-water cycle and to assure that no MDEA is present in the demineralized water (as this can form organic acids under boiler conditions), so it is discharged via the wastewater. Therefore, other technologies than IEX are investigated for the possible re-use of this condensate stream.

1.2. Goal

Desalination of the streams was investigated by means of three different techniques: electrodialysis (ED), reverse osmosis (RO), membrane stripping or distillation (MS/MD), depending on the configuration. ED is an upcoming technique, in which an electrochemical potential difference is used to achieve separation through ion exchange membranes (IEM). RO is a state of the art technique using a hydraulic pressure difference to overcome the osmotic pressure between two solutions and produce a clean permeate. The most recent techniques are MS and MD, where a difference in pH (MS) or a difference in temperature (MD) is applied to achieve transport through a hydrophobic membrane (either transport of the contaminants or of the pure water, depending on the operational mode).

The main goal for Yara Sluiskil B.V. is on the one hand to reuse the treated process condensates in other cycles (e.g. boiler feed water), in order to reduce the use of demineralized water and to decrease the water footprint. On the other hand, the goal is to investigate (especially for the C1 stream) whether the ammonium nitrate that is separated from the condensate can be concentrated and recovered from the process condensate to be reused after treatment, resulting in a much lower environmental impact and cost of discharge. This way, both the polished and the concentrated stream can be re-used to achieve a closed loop in the end.

In general, the specifications for boiler feed water produced by *Evides Industriewater* are given in **Table 1**. The produced water quality with the different water treatment technologies should be able to meet these specifications. Concerning Total Organic Carbon (TOC) the aimed value is more or less 100 ppb.

Table 1. Specifications for the production of boiler feed water.

	Unit	Phosphate treatment	All-volatile
Operating pressure	bar	40 - 100	total range
Conductivity at 25°C	μS/cm	< 2	-
Cation conductivity at 25°C	μS/cm	-	< 0.2
pH at 25°C (after addition of neutraliser)	-	9 - 9.2	> 9.2
Total hardness (calcium, magnesium)	ppm CaCO ₃	< 0.05	0
Na + K	ppm	not specified	< 0.01
Fe	ppm	< 0.02	< 0.02
Cu	ppm	< 0.005	< 0.003
SiO ₂	ppm	not specified	< 0.02
O ₂	ppm	< 0.02	< 0.01
Oil	ppm	< 0.5	< 0.2
TOC	ppm	< 0.5	< 0.2

2. Technologies of interest

2.1. Electrodialysis

Electrodialysis is a desalination technique in which separation of ions and water is achieved by applying an external potential difference across semipermeable membranes. Here, Anion Exchange Membranes (AEM) and Cation Exchange Membranes (CEM) are altered in the ED element in order to establish desalination of the diluate stream and transport the ions to the concentrate. A general overview of the ED layout is provided in the **Figure 1**. For more details about the operation of the ED module, consult the project document 'Functional Description EDR' [1].

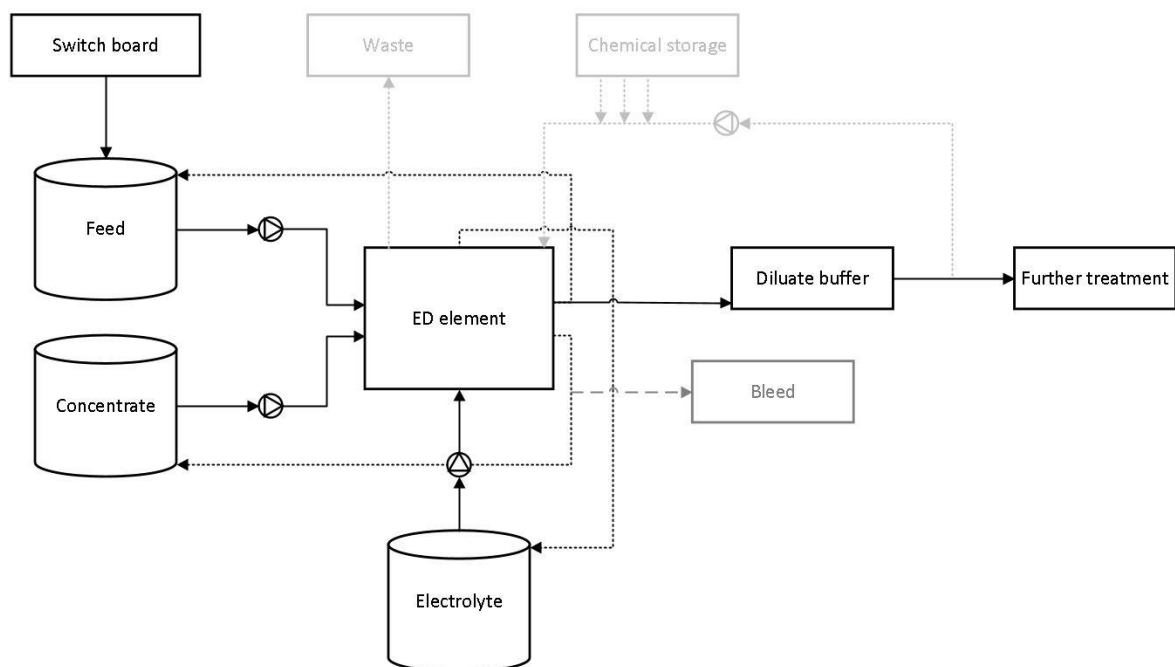


Figure 1. Schematic overview of the ED module.

A more in-depth view on the working mechanism of the ED module, with the respective cell pair configuration, is shown in **Figure 2**. The operating principle of ED: when a watery feed solution, for example containing ammonium nitrate, is sent through the stack and a direct current is applied, the positively charged ammonium ions will migrate towards the cathode and the negatively charged nitrate ions towards the anode. The nitrate ions can pass the positively charged AEM, but are retained by the positively charged CEM. The opposite is true for the ammonium ions. This results in an increase of ions in the concentrate stream and simultaneously a decrease of ions in the diluate stream. The ED 1000A module from PCell consisted of 25 cell pairs.

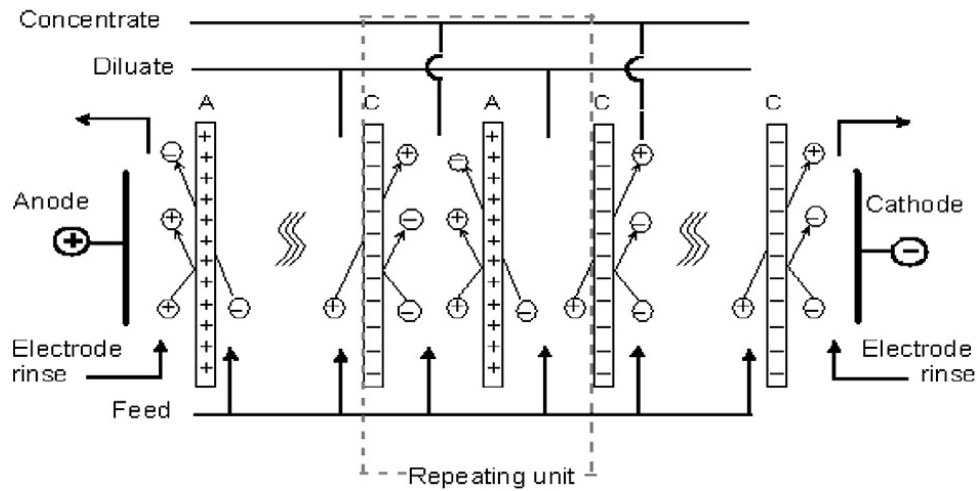


Figure 2. Separation mechanism in an ED module [2].

The electrode rinse in **Figure 2** is the electrolyte, which was a solution of 1M NaNO₃.

2.2. Reverse osmosis

In Reverse Osmosis (RO), a pressure gradient leads to the separation of solutes and water 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 to 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 biofouling and reduce potential clogging of the spacer by small particles. A general overview of the RO layout is provided in the **Figure 3**. For more details about the operation of the RO module, consult the document ‘Functional Description RO’ [3].

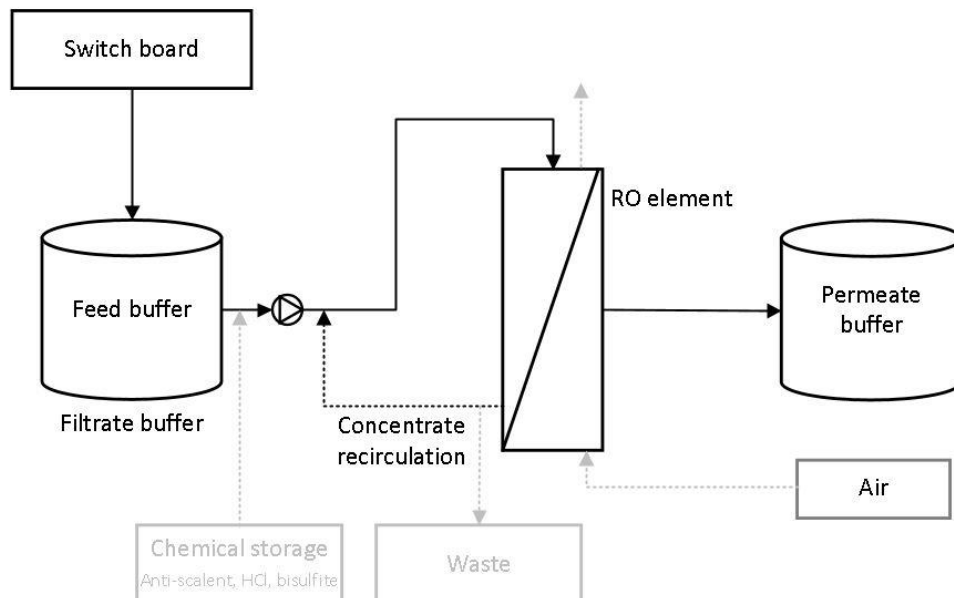


Figure 3. Schematic overview of the RO module.

Whenever a higher recovery is applied, the concentrate recirculation is increased in order to have a sufficient longitudinal flow rate and a good mixing.

2.3. Membrane distillation and stripping

Membrane distillation is an example of thermally-driven membrane processes. The hydrophobic membrane only allows passage of volatile (water vapour, ammonia, ...) or hydrophobic substances (e.g. organic solvents), while retaining all other 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 an extra driving force gradient other than a temperature gradient (e.g., often a pH gradient);
- Direct Contact MD: the membrane acts as the only barrier between feed and receiving phase and a temperature gradient is used as driving force;
- Air-Gap MD: an additional air gap and cooling wall are installed between the membrane and the cooling phase, but temperature is also the driving force.

For the case study at Yara, the MD module was used in the MS mode and in the DCMD mode. A general overview of the MD layout is provided in the **Figure 4**. For more details about the operation of the MD module, consult the document 'Functional Description MD' [4].

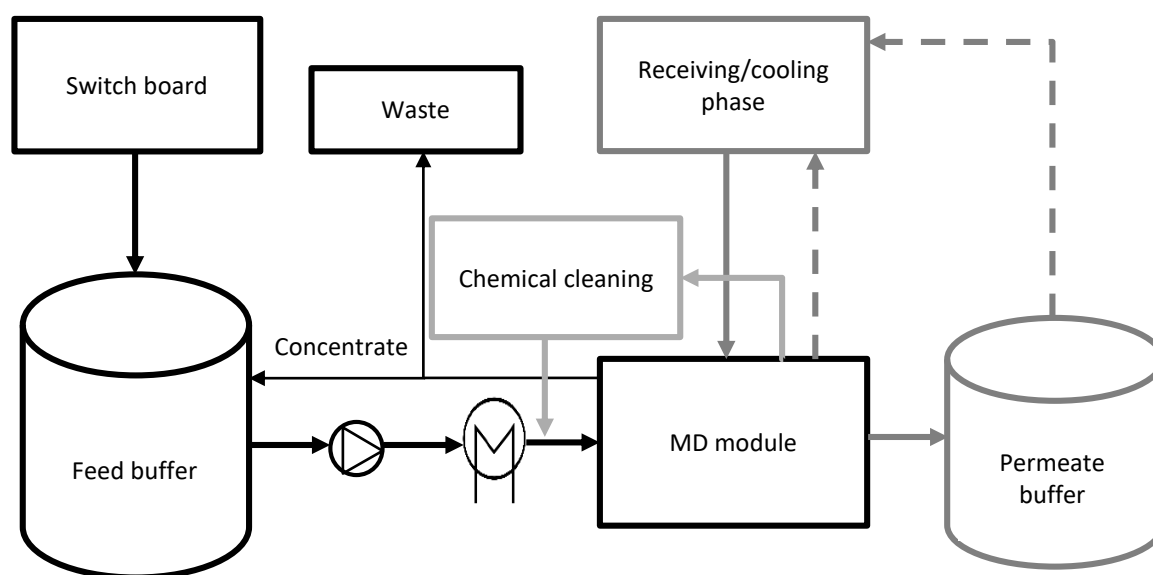


Figure 4. Lay-out of the MD module.

A more in-depth view on the working mechanism of both MD and MS is shown in **Figure 5**. Here, the difference in temperature or pH is of most importance, respectively.

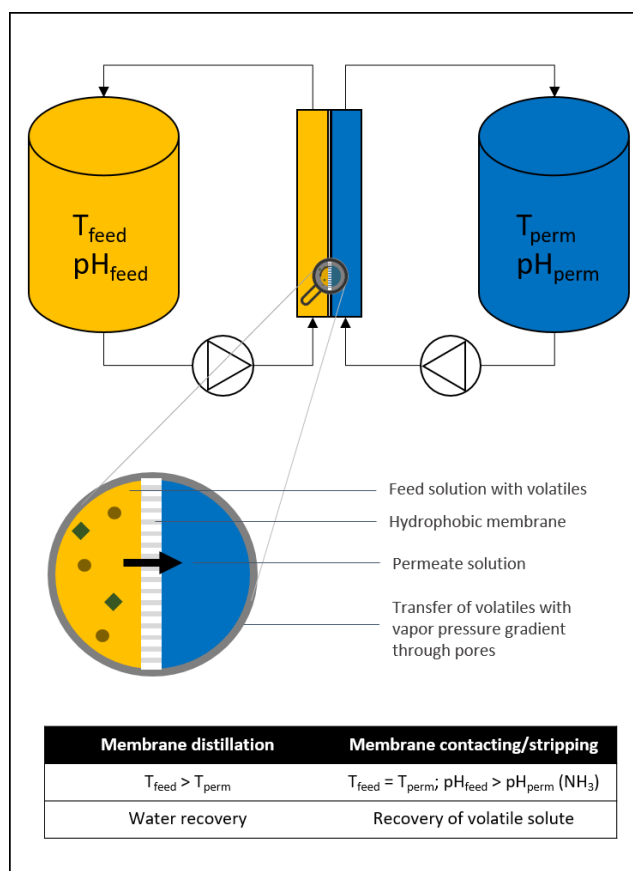


Figure 5. Schematic representation of membrane distillation and stripping, based on a difference in temperature or pH.

3. Materials and Method

3.1. Electrodialysis

In **Figure 1** 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 amperage were continuously measured online.

On the SR800 stream (C1), ED was tested in both Feed and Bleed mode and Continuous mode. For the Feed and Bleed mode, the setting for the desired product quality was 10 $\mu\text{S}/\text{cm}$. In Continuous mode, the maximal concentrate conductivities varied from 800 $\mu\text{S}/\text{cm}$ to 2500 $\mu\text{S}/\text{cm}$.

On the CO₂-condensate (C2), also feed and bleed mode and continuous mode were tested. For the feed and bleed mode, the set point of the desired product quality varied from 25 $\mu\text{S}/\text{cm}$ to 800 $\mu\text{S}/\text{cm}$ with a maximal concentrate conductivity of 5000 $\mu\text{S}/\text{cm}$. Additionally, 7500 and 9500 were tested as maximal concentrate conductivities. In the continuous mode, the maximal concentrate conductivities of 5000, 7500 and 9500 were tested.

3.2. Reverse osmosis

In **Figure 3** the scheme of the RO set-up is shown. The RO membrane was a Dow Filmtec LC HR-4040 (Lenntech, The Netherlands), 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.

On both the SR800 stream and the CO₂-condensate, three recoveries were tested (75-80-85%) with a permeate flux of 20 l/m².h each for 3 consecutive days. An additional test was performed with a recovery of 85% and a permeate flux of 25 l/m².h on the C1. Daily samples were taken on which ammonium, nitrate and TOC were measured. No chemicals were dosed.

3.3. Membrane distillation and membrane stripping

In **Figure 4** the scheme of the MD set-up is shown. The MD membrane was a polypropylene membrane in a spiral wound module (Aquistill, the Netherlands). The active membrane area was 7.2 m². Further details on the module are confidential. The feed and permeate flow was 800 L/h. The feed was continuously recirculated and drained every 10 minutes (time depends on setting), with a flow of 1500L/h. The permeate was continuously recirculated and excess was drained by an overflow.

On the SR800 stream membrane distillation at 55°C feed temperature was tested. The permeate temperature was kept constant at 32.5 ± 2.5 °C. On the CO₂ condensate, membrane stripping was tested at 40°C and 50°C.

3.4. Economic evaluation

An economic analysis was performed for the different water technologies for both water streams (SR800 and CO₂-condensate) 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

4.1. SR800 stream (C1)

This stream is a steam condensate at the Yara site, which is normally treated by *Evides Industriewater* at the Biesbosch IEX street in order to remove the access ammonia nitrate. The SR800 stream mainly contains NH₄⁺ and NO₃⁻ ranging from 10-15 mg/L and 35-50 mg/L respectively, together with a small amount of iron (1.8 mg/L). The TOC content on average was 62 mg/L. In general, sulphate, chloride, acetate and formate are present in very small amounts (µg/L range). Based on the results from a master thesis conducted prior to the pilot tests [5], a more detailed average composition of the SR800 stream is given in Appendix. The SR800 stream was treated with three different water desalination technologies, namely EDR, RO and MD. The results of the pilot-scale experiments will be discussed in more detail in the following paragraphs.

4.1.1. Electrodialysis

The EDR technique was used in both Feed and Bleed and Continuous mode. For the SR800 stream no current-voltage plots are made, as the current was too low for accurate measuring. During Feed and Bleed mode, the diluate out was recirculated to the feed tank as long as the set specifications for the product quality were not met. Whenever the desired product quality was reached, a constant amount of volume of the diluate out was bled and fresh C1 was added to the feed tank. In this way the feed water passed through the ED module multiple times in order to increase treatment efficiency. In comparison, the Continuous mode is a once-through system, where the diluate out is never recirculated.

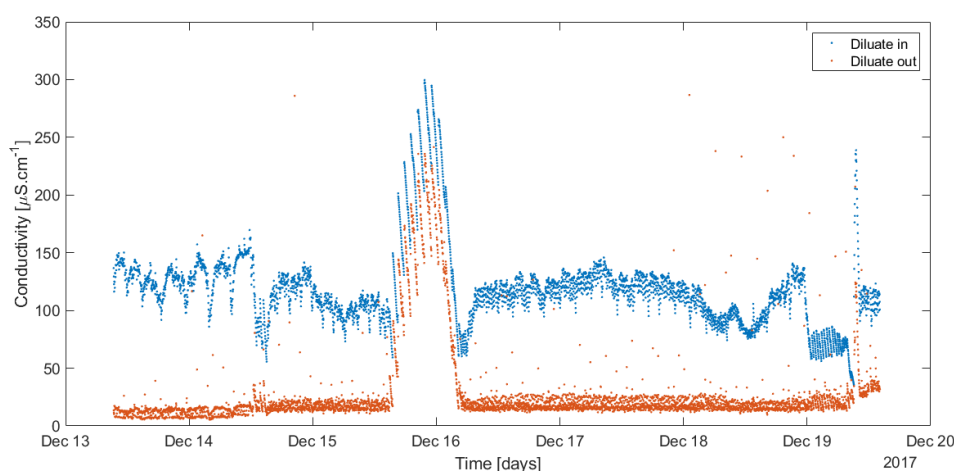


Figure 6. Conductivity of diluate in and out during EDR in Feed and Bleed mode. The maximum product quality was set at 10 $\mu\text{S}/\text{cm}$.

Figure 6 shows that despite the fact the incoming water quality (diluate in) is not constant, the product quality (diluate out) is almost stable (the sudden increase in feed water conductivity not taken into account, this was due to another influent water (Biesbosch surface water)). Therefore, EDR is able to produce a constant product quality, independent of the quality of the feed water. During Feed and Bleed mode, the average conductivity of the diluate in and out was 130 and 14 $\mu\text{S}/\text{cm}$, respectively, resulting in a removal efficiency of 89% based on conductivity. The specific removal efficiencies for NH_4^+ and NO_3^- varied between 72-88% and 76-91%, respectively. Ion analyses of diluate and concentrate are given in **Table 2**, with a focus on ammonium and nitrate. The EDR technique did not remove any organic matter.

Table 2. Analyses of the diluate and concentrate during EDR in Feed and Bleed mode.

	Diluate in			Diluate out			Concentrate in			Concentrate out		
	EC [μ S/cm]	NH ₄ ⁺ [ppb]	NO ₃ ⁻ [ppb]	EC [μ S/cm]	NH ₄ ⁺ [ppb]	NO ₃ ⁻ [ppb]	EC [μ S/cm]	NH ₄ ⁺ [ppb]	NO ₃ ⁻ [ppb]	EC [μ S/cm]	NH ₄ ⁺ [ppb]	NO ₃ ⁻ [ppb]
	100	10.1	39.8	9.3	1.2	4.3	304	25.3	123	239	31.2	153
	148	6.2	39	10.3	1.2	3.5	278	12.9	82	408	21.2	133
	79	4.7	30.9	18.1	1.3	7.3	1376	37.5	575	1488	41.4	612
Average	105 \pm 25.9	7.0 \pm 2.3	36.6 \pm 4.0	12.3 \pm 6.5	1.2 \pm 0.1	5.0 \pm 1.6	296.7 \pm 64.3	25.2 \pm 10.0	260 \pm 223	284.1 \pm 77.3	31.3 \pm 8.2	299.3 \pm 221

A product quality set-point of 10 μ S/cm was set. This resulted in a diluate bleed of approximately 13 L about every 10 min, resulting in a production of 78 L/h of product water or a water efficiency of 85-89%.

The product quality during Continuous mode was worse compared to the Feed and Bleed mode, as no recirculation was performed and this mode can be seen as a single-pass treatment. However, the lower product quality is probably not only caused by the difference in operation mode, but also by the fact that the incoming water quality was worse. The average conductivity of the diluate in and out was 234 and 51 μ S/cm, respectively. The conductivity of the diluate in was about 100 μ S/cm higher compared to the one during Feed and Bleed mode. Based on the conductivity the removal efficiency was 78%.

The Continuous mode was performed with different maximum concentrate conductivity set points, namely 800, 1100, 1400, 1700, 2000 and 2500 μ S/cm, in order to investigate the highest possible water efficiency and the effect on the product quality. From Figure 7, it is clear that the variability in incoming water quality had little to no effect on the product quality. In addition, the variation in maximum concentrate conductivity had no obvious effect. Therefore, it is recommended to operate EDR at the highest maximum concentrate conductivity in order to increase the water efficiency.

Ion analyses of diluate and concentrate are given in **Table 3** for experiments with different maximum concentrate conductivity, with a focus on ammonium and nitrate. Again, the EDR technique did not remove any organic matter.

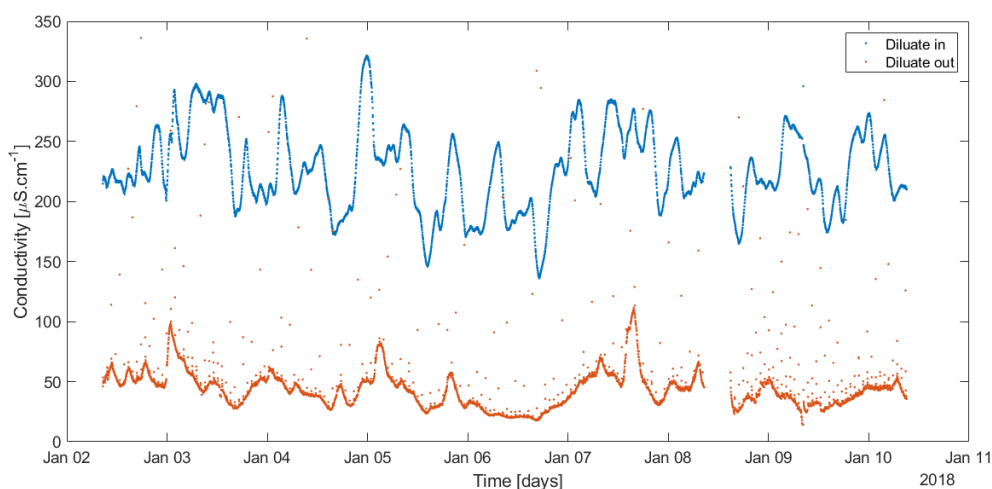


Figure 7. Conductivity of diluate in and out during EDR in Continuous mode at a constant current of 0.3 A.

The specific removal efficiencies for NH_4^+ and NO_3^- varied between 43-72% and 35-76%, respectively at a constant current of 0.3 A. In general, the removal efficiencies are lower compared to the Feed and Bleed mode and tend to have a higher variability. The maximum concentrate conductivity had no clear effect on the removal efficiencies.

Table 3. Analyses of the diluate and concentrate during EDR in Continuous mode. Max. stands for the maximum concentrate conductivity. No average values are given for the concentrate as these values are not representative due to the different maximum concentrate conductivity set-points.

Max.	Diluate in			Diluate out			Concentrate in			Concentrate out		
	EC [µS/cm]	NH_4^+ [ppm]	NO_3^- [ppm]	EC [µS/cm]	NH_4^+ [ppm]	NO_3^- [ppm]	EC [µS/cm]	NH_4^+ [ppm]	NO_3^- [ppm]	EC [µS/cm]	NH_4^+ [ppm]	NO_3^- [ppm]
800	210	23.6	85.3	51.5	8.1	24.9	636	57.8	263	731	69.9	322
1100	182.9	4.6	11.7	28.6	4.2	10.1	989	63.9	340	1096	72.1	385
1400	191.2	11.6	56.8	25.6	3.7	15.5	1259	55.4	371	1379	61.8	407
1700	249.3	13.4	70.4	40.5	6.1	18.5	1508	106	552	1697	113	600
2000	232.2	19.2	97.5	56.2	10.9	63.4	1813	93	677	1910	108	243
2500	202.6	16.2	80.3	45.7	5.6	25.1	3820	141	1429	4050	159	1397
Average	218 ±39.48	13.3 ±5.0	66.1 ±22.5	39.3 ±10.0	6.21 ±2.42	28.3 ±19.6	-	-	-	-	-	-

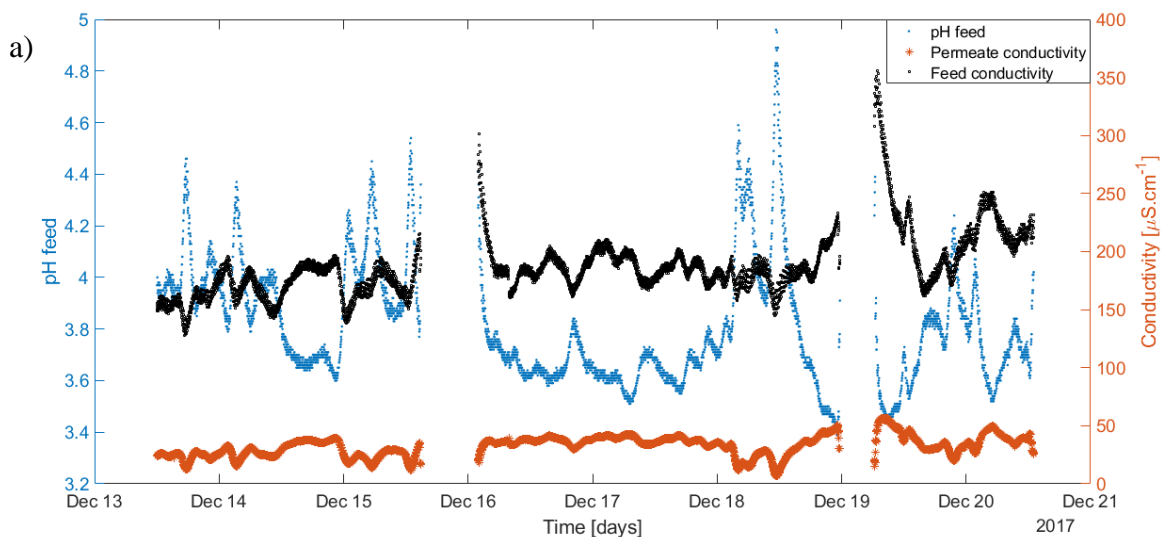
The water efficiencies for the Continuous mode experiments depended on the maximum concentrate conductivity and ranged from 89% to 95%, for a maximum concentrate conductivity of 800 and 2500 $\mu\text{S}/\text{cm}$, respectively. The water efficiency is higher compared to the Feed and Bleed mode as in the Continuous mode treated water is continuously produced. The impact on the product quality of the Continuous mode cannot be determined unambiguously because the incoming water quality for both modes was not the same (the average diluate in conductivity was twice as high during the Continuous mode, compared to the Feed and Bleed mode, respectively 105 and 218 $\mu\text{S}/\text{cm}$). However, the product quality is more than three times worse during Continuous mode based on conductivity alone. The concentration for both ammonia and nitrate is more than 5 times higher.

For both modes, the diluate out conductivity cannot meet the desired value for boiler feed water. A double-pass EDR will not be sufficient, as EDR is less efficient at lower feed concentrations. A polishing step, such as a mixed bed ion exchange treatment, would be necessary to achieve these requirements.

Note that the composition of the EDR membranes changed during the operation at Yara, most probably the backbone structure reacted with the composition of the incoming feed water. However, it had no effect on the performance of the membranes.

4.1.2. Reverse osmosis

Treatment of the C1 stream with RO was conducted at different recovery set points. An overall performance graph is given in **Figure 8**. The following graphs will discuss different parameters in more detail.



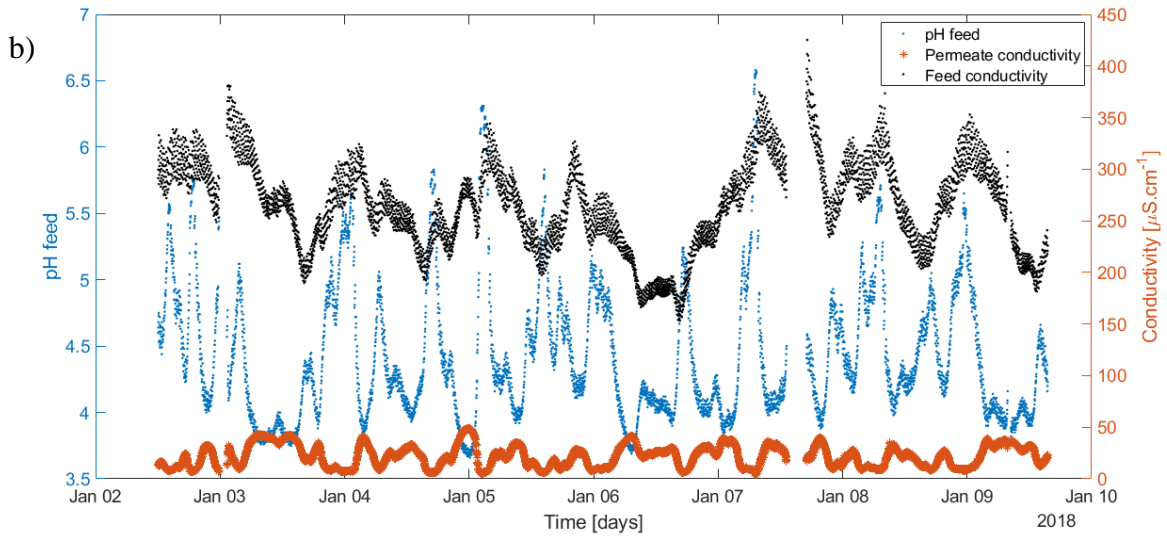


Figure 8. Overall performance of the RO treatment on the SR800 stream.

Figure 9 shows that the permeate conductivity is clearly correlated with the pH of the feed, whereas there is no clear correlation with the conductivity of the feed. The high conductivity of the permeate is most probably caused by H^+ -ions, and in that way the correlation with the pH can be explained. Almost 80% of the permeate conductivity is explained by the presence of H^+ -ions. In **Table 4**, the ion analyses are given. The specific retention capacities for NH_4^+ and NO_3^- varied between 97-99% and 66-92%, respectively. During the RO treatment, TOC was also partially removed (27-66%).

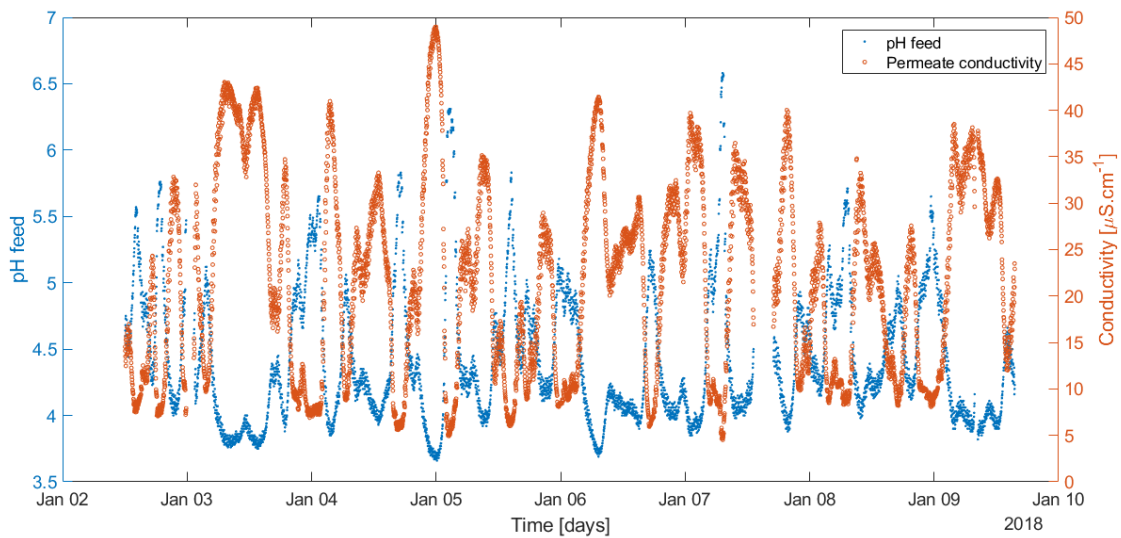


Figure 9. Correlation between permeate conductivity and the pH of the feed versus time.

Table 4. Analyses of feed, permeate and concentrate during RO treatment at different recovery ratios (R).

R [%]	Feed					Permeate				Concentrate			
	pH	EC [μS/cm]	TOC [ppb]	NH ₄ ⁺ [ppm]	NO ₃ ⁻ [ppm]	EC [μS/cm]	TOC [ppb]	NH ₄ ⁺ [ppm]	NO ₃ ⁻ [ppm]	EC [μS/cm]	TOC [ppb]	NH ₄ ⁺ [ppm]	NO ₃ ⁻ [ppm]
75	3.98	214	64.5	17.8	78.5	118.7	25	0.2	17	226.6	87	23	94.4
	3.99	229.2	61.7	18.6	82.8	128.2	25.7	0.5	18.3	247.1	72	21.5	91.3
	3.86	259.3	77	20	91.3	152.7	39	0.2	17.4	275.5	98.3	21.4	17.4
80	4.5	432.2	111	49.3	191	87.7	38	1.7	15.6	503.5	127	62.3	244
	3.86	416.4	71.3	40.6	173	203.3	45.3	0.4	29.5	473.7	83.3	32.2	141
	4.01	412.9	78.7	40.5	170	170.9	37	0.8	24.5	462	77.3	45.2	183
85	4.18	366.1	77	40	158	129.9	44	0.7	19.3	418.6	100	48	190
	3.95	302.6	59.7	25.5	115	165.8	43.3	0.3	24.1	333.1	71.3	34	143
Average	4.13 ±0.40	319.90 ±90.61	75.1 ±12.6	29.9 ±11.4	129.9 ±48.6	140.9 ±52.1	38.2 ±10.8	0.8 ±0.9	20.7 ±6.3	373.3 ±90.5	83.6 ±16.2	37 ±16.8	159 ±94.1

Most of the time HNO₃ is added to the SR800 stream to lower the pH in order to prevent scaling (CaCO₃ and MgCO₃) on the ion exchange resins in the water treatment plant of *Evides Industriewater*. The pH has a clear effect on the retention efficiency of ammonium; the lower the pH, the higher the retention efficiency and the lower the concentration in the permeate. The opposite is true for the nitrate concentration. The latter is partially explainable due to the fact that with the addition of HNO₃ a higher concentration gradient exists across the membrane, leading to lower rejection efficiencies for HNO₃ at lower pH. The higher retention capacity for ammonium at lower pH might also be correlated with the zeta-potential of the RO membrane, but further research is needed to make any definite statement about this hypothesis. Whenever another treatment method could be used instead of ion exchange, a re-evaluation can be made on the necessity of HNO₃ addition. It might be possible that EDR, RO or MD needs less chemical addition, which can result in a decrease or elimination of the acid cost.

As could be seen in **Figure 9**, the lower the pH of the feed, the higher the permeate conductivity. This can be explained by the findings of the ion analyses. Whenever the pH of the feed is low, more HNO_3 is transported through the membrane, causing an increase in permeate conductivity as HNO_3 gives rise to a higher conductivity compared to NH_4NO_3 . The same conclusion can be drawn from Figure 8, where the nominal salt passage (NSP) shows a clear relation with the pH of the feed, the same pattern is established as between the permeate conductivity and the feed pH. However, the NSP in the figures below is very high and is not representative of a good working RO procedure.

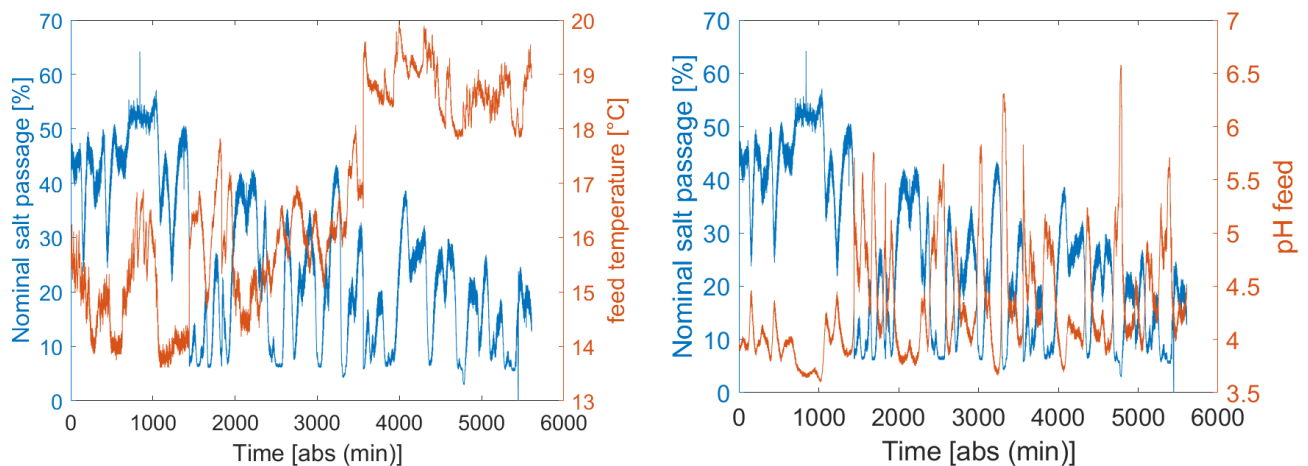


Figure 10. Relation between nominal salt passage and the temperature and the pH of the feed in absolute time units.

The NSP values in **Figure 10** were calculated from the permeate conductivity and should therefore be corrected for pH, or the presence of H^+ -ions, as discussed above. The corrected NSP values are given in **Figure 11**.

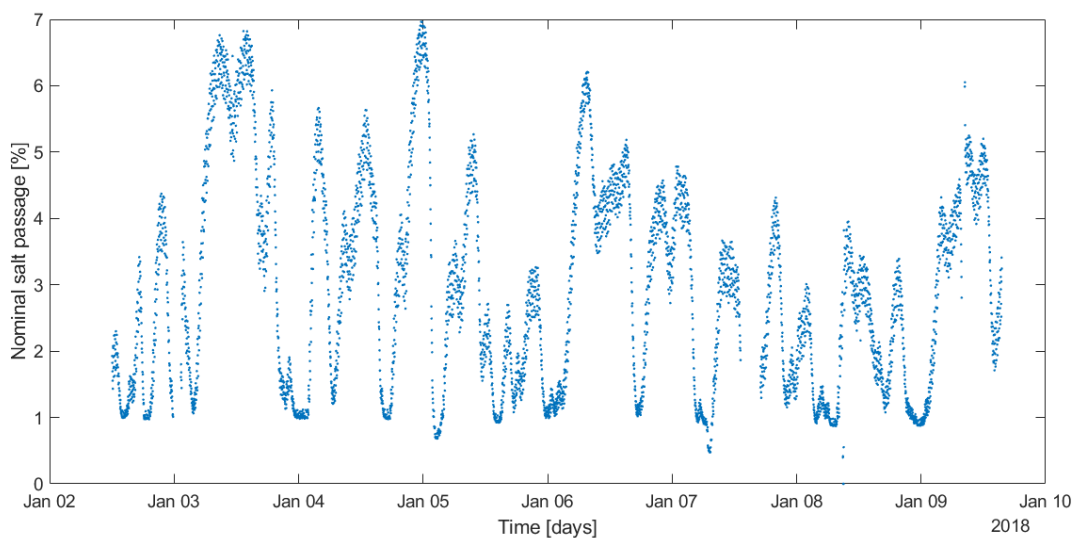


Figure 11. The corrected NSPT values for the RO treatment on the SR800 stream.

Note that the measured conductivity is almost always lower than the calculated conductivity, based on the ion analyses. Probably, there is another compound in the SR800 stream which influences the conductivity. This might be a small organic acid, such as formate, acetate or CO₂.

From **Figure 12**, it can be seen that the Mass Transfer Coefficient (MTC) is not influenced by the recovery. The recovery in the pilot-scale set-up has no effect on the water flux, but it has an effect on the recirculation of the concentrate. The permeate flux was fixed at 20 L·m⁻²·h⁻¹, only the ratio of concentrate which was discarded and recirculated changed with different recoveries. The higher the recovery and thus the water efficiency, the higher the recirculation of concentrate and the lower the intake of fresh incoming water to the RO module. If a higher flux was desired, the energy consumption would have increased. This principle is explained in more detail in **Table 5**.

Although the recovery did not show any influence on the MTC, it should be mentioned that the runtime of the experiments was rather short. During this period, no fouling nor scaling occurred, while this might happen when the runtime is increased to weeks or even months.

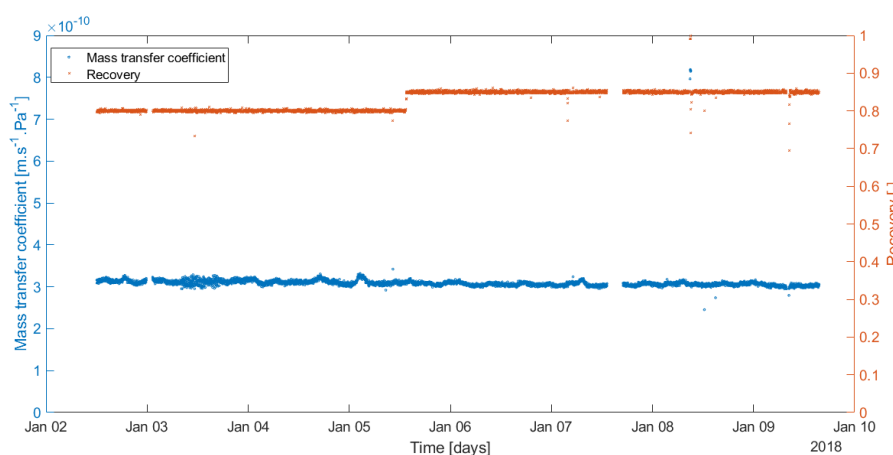


Figure 12. The Mass Transfer Coefficient for the different recovery ratios during RO treatment.

Table 5. Explanation of the RO recovery in terms of the respective stream flows.

Recovery [%]	Flux [L/m ² .h]	Q feed [L/h]	Q permeate [L/h]	Q discarded concentrate [L/h]
75	20	232	175	57
80	20	218	175	43
85	20	205	175	30
85	25	273	219	54

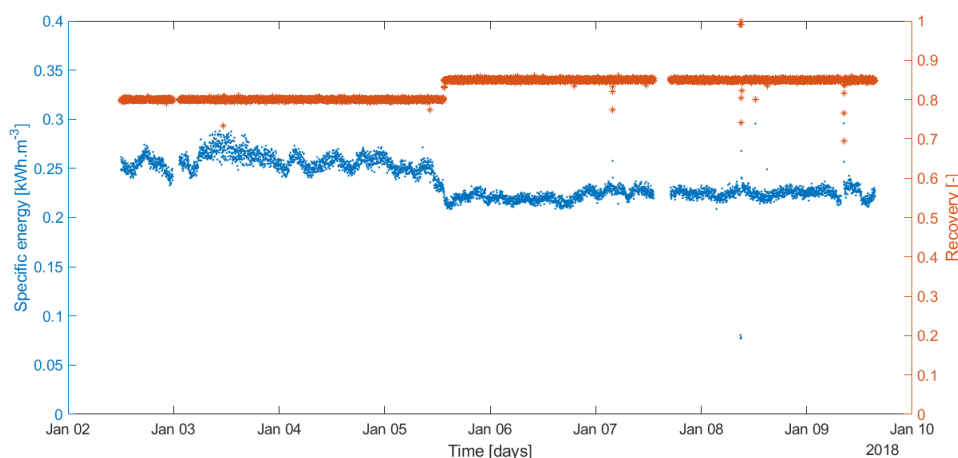


Figure 13. Specific energy requirement for the RO treatment at different recoveries.

The Specific Energy Requirement (SEC) was only based on the pressure drop over the membrane. In fact, the depicted SEC refers only to the required pumping energy. A higher recovery results in a lower SEC, as this implies a higher production of treated water. Nevertheless, a higher pressure needs to be maintained in order to obtain a higher recovery.

4.1.3. Membrane distillation

During a preliminary test, the performance of MD was investigated at a feed temperature of 55°C and a permeate temperature of 35°C. The results are given in the table below.

Table 6. Preliminary MD test at a feed and permeate temperature of 55°C and 35°C, respectively.

Time [h]	Feed			Permeate		
	EC [$\mu\text{S}/\text{cm}$]	NH_4^+ [ppb]	NO_3^- [ppb]	EC [$\mu\text{S}/\text{cm}$]	NH_4^+ [ppb]	NO_3^- [ppb]
0	265	21.9	107	39	4.2	12.5
5	360	31.4	151	23	2.4	6.5
24	623	37.8	182	0	0.6	1.4
26.5	591	48	232	0	0.7	0.6
28	611	48.2	235	0	1	0.8

At the start of the experiment, the water solution at the permeate side was RO permeate due to the absence of fresh demineralized water, which is the reason the concentration for both ammonia and nitrate was not zero. During the experiment, these concentrations decreased, meaning that only water was transported through the MD membrane and both compounds were retained completely. This resulted in a dilution of the RO permeate and the associated low concentrations of NH_4^+ and NO_3^- . The water flux obtained at these parameter settings was 14 L/h or 1.94 L/m².h⁻¹. With more heating and cooling capacity a higher flux could

be obtained. If MD seemed a plausible technique after the economic evaluation, this might be of interest to investigate in more depth.

After the preliminary experiment, a longer continuous experiment was performed and showed the same general conclusions. Concerning TOC, the results are not conclusive, but it is expected that some volatile organic components were transported through the MD membrane, as the TOC concentration in the permeate did not show a clear decreasing trend. The water efficiency ranged between 68-75%. Despite the lower water efficiency compared to EDR and RO, the product quality of the MD permeate was the best, as no ammonia or nitrate went through the membrane. With this technology, the specifications for boiler feed water can be met without any additional treatment.

4.1.4. Economic evaluation of the SR800 stream

For each technology, a maintenance cost of 6% of the total investment per year was assumed. 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 economic analysis for EDR was based on a quote from 2013 taking into account a total inflation of 8% until the year 2017. The EDR membranes were expected to have a life-time of 10 years, whereas for the electrodes this is only 3 years. The economic analysis for RO was based on the knowledge of *Evides Industriewater*. Here, the average and maximum flow rate were set at 50 and 60 m³/h.

Table 7. Cost estimation for treatment of the SR800 stream by EDR.

OpEx	Amount	Price	Costs/year
Energy	219 000 kWh/year	€ 0.07/kWh	€ 15 330.00
HCl			€ 329.96
NH ₄ Cl			€ 5 329.00
Maintenance			€ 37 944.14
Membrane and electrode replacement			€ 55 020.63
Total			€ 113 953.73
CapEx	Amount	Price	Costs
ED membranes and electrodes	7	€ 72 554.68/stack	€ 507 882.74
Stack accessoires			€ 25 000.00
Pumps			€ 20 000.00
Electric supply			€ 50 000.00
Chemical storage and dosing	2	€ 8000/unit	€ 16 000.00
CIP tank & pump			€ 12 000.00
Buffers			€ 10 000.00
Piping and valves			€ 13 000.00
Instrumentation			€ 20 000.00
Civil			€ 35 000.00
Process automation			€ 50 000.00
Total			€ 758 882.74

Table 8. Cost estimation for treatment of the SR800 stream by RO.

OpEx	Amount	Price	Costs/year
Energy	162 798 kWh/year	€ 0.07/kWh	€ 11 395.86
HCl			€ 41.77
NaOH			€ 67.74
Maintenance			€ 11 340.00
Module replacement			€ 4 800.00
Total			€ 27 645.38
CapEx	Amount	Price	Costs
RO modules		€ 600	€ 24 000.00
Pressure vessels	10	€ 600/piece	€ 6 000.00
HP pump			€ 25 000.00
Chemical storage and dosing			€ 16 000.00
CIP tank & pump	2	€ 8000/unit	€ 12 000.00
Buffer			€ 8 000.00
Piping and valves			€ 13 000.00
Electrics and instrumentation			€ 20 000.00
Civil			€ 15 000.00
Process automation			€ 50 000.00
Total			€ 189 000.00

The economic analysis for MD was based on a recent quote from Aquastill (23/08/2018).

Table 9. Cost estimation for treatment of the SR800 stream by MD.

OpEx	Amount	Price	Costs/year
Electric energy	125 201 kWh/year	€ 0.07/kWh	€ 8 764
HCl			€ 500
NaOH			€ 500
Maintenance			€ 80 242
Membrane replacement			€ 232 169
Total			€ 322 176
CapEx	Amount	Price	Costs
MD membranes	464	€ 2500/module	€ 1 160 847
Skid accessoires			€ 50 000
Pumps			€ 20 000
Electric supply			€ 100 000
Heating and cooling equipment		€ 8000/unit	€ 120 000
Chemical storage and dosing	2		€ 16 000
CIP tank & pump			€ 12 000
Buffer			€ 8 000
Piping and valves			€ 13 000
Instrumentation			€ 20 000
Civil			€ 35 000
Process automation			€ 50 000
Total			€ 1 604 847

The MD membranes are expected to have a life-time of 5 years. The source for heat recuperation was not included. Thermal energy needed for heating and cooling amounted to 136 550 and 125 201 MWh/year, respectively.

From the economical evaluation it is clear that both EDR and MD are not ready to be used at large-scale. The initial investment costs are too high and are not able to compete with RO for this particular application. For MD, the main reason is the high amount of MD modules needed in order to produce a desired product volume due to the low membrane flux which was obtained during the pilot-scale experiments. In addition, the price for each MD module or EDR stack is much higher compared to a single RO module. If the market is not willing to invest in these techniques in order to reduce the initial costs for the membranes and the stacks, these techniques will never be used for large-scale operations for the production of boiler feed water, starting from feed water as investigated here. The main applications which are able to use these 'expensive' technologies are highly specific case studies where RO or other state-of-the-art technologies are not able to solve the problem.

As the ammonium nitrate concentration in the SR800 stream is low, recovery of this component is unlikely with the investigated technologies. The scope of the investigation was mainly the search for a more efficient and more ecological alternative in comparison of the currently used IEX technique. The driving force was to minimize the discharge of these components, water recuperation was a secondary target. If product quality, production efficiency and the cost of investment are taken into account, RO is the only technology which can

be considered for future use. However, it should be mentioned that RO alone will most probably not be enough to meet the boiler feed water specifications. An additional mixed bed ion-exchange step on the RO permeate can offer the solution. The question remains whether the investment for building and operating a new technology is an option, as for the SR800 stream the IEX train from *Evides Industriewater* can handle it. If the main driver is indeed the discharge problem, the latter question is less important. One uncertainty is the dosage of HNO_3 for the current pH regulation in order to prevent scaling. In RO, scaling must also be prevented but other options are possible, which can lead to a better performance of the RO.

4.2. CO₂-condensate stream (C2)

The C2 stream was treated with three different water desalination technologies, namely EDR, RO and MS. The results of the pilot-scale experiments will be discussed in more detail in the following paragraphs.

4.2.1. Electrodialysis

The main objective for the C2 stream is the removal of ammonia and also separation of the alcohols and MDEA from the condensate stream. Recovered components can be reused in the production process. This is the main reason that in the experiments for Continuous mode the maximum concentrate conductivity was also examined along with the removal of ammonia from the diluate stream.

Fout! Verwijzingsbron niet gevonden. **14** shows the conductivity of the diluate stream in and out of the EDR module in Feed and Bleed mode. The vertical lines in this figure separate the applied value for the maximum product quality. In general, the removal for NH_4^+ and NO_3^- based on conductivity is around 60%. **Figure 15** shows the conductivity of both diluate and concentrate stream in and out during Continuous mode. The average removal efficiency based on conductivity is again around 60%. In the situation with the same feed, a higher removal in Feed and Bleed mode is expected than in Continuous mode. However, in this case the same range for removal efficiencies is observed in both modes. The main reason for achieving the same removal efficiency is related to the higher conductivity of the feed stream into the EDR module during Continuous mode.

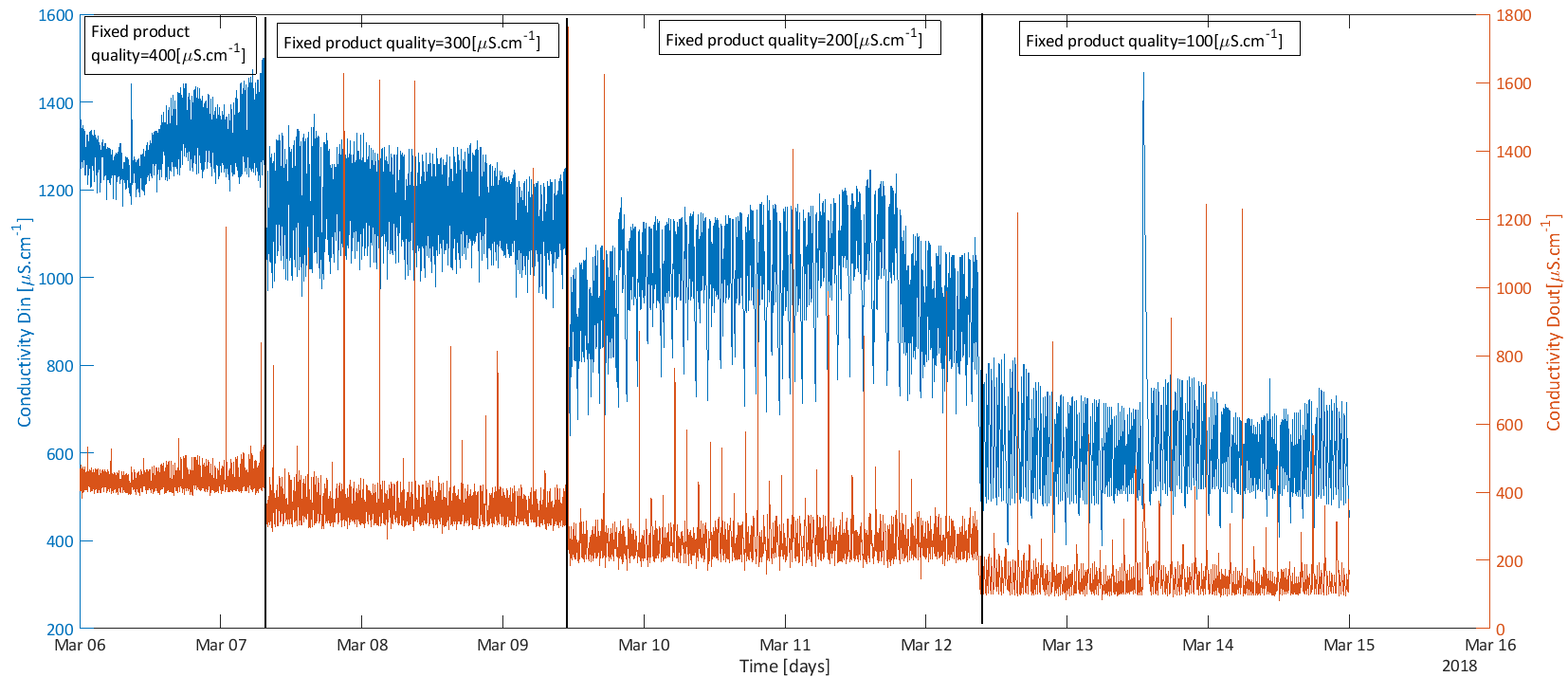


Figure 14. Conductivity of diluate in and out during Feed and Bleed mode, vertical lines are separating the experimental area with fixed product quality.

The reason for the decreasing conductivity over the experiments with a lower set product quality is the definition of diluate in. The feed water, which is here the diluate in, is not the same over the experiments as a large amount of the feed water is recirculated from the diluate out. The lower the set point of the product quality, the more the diluate out is recirculated to the feed water tank (diluate in) and the less fresh water from the CO₂-condensate is taken in. This results in a lower water efficiency at a lower set product quality.

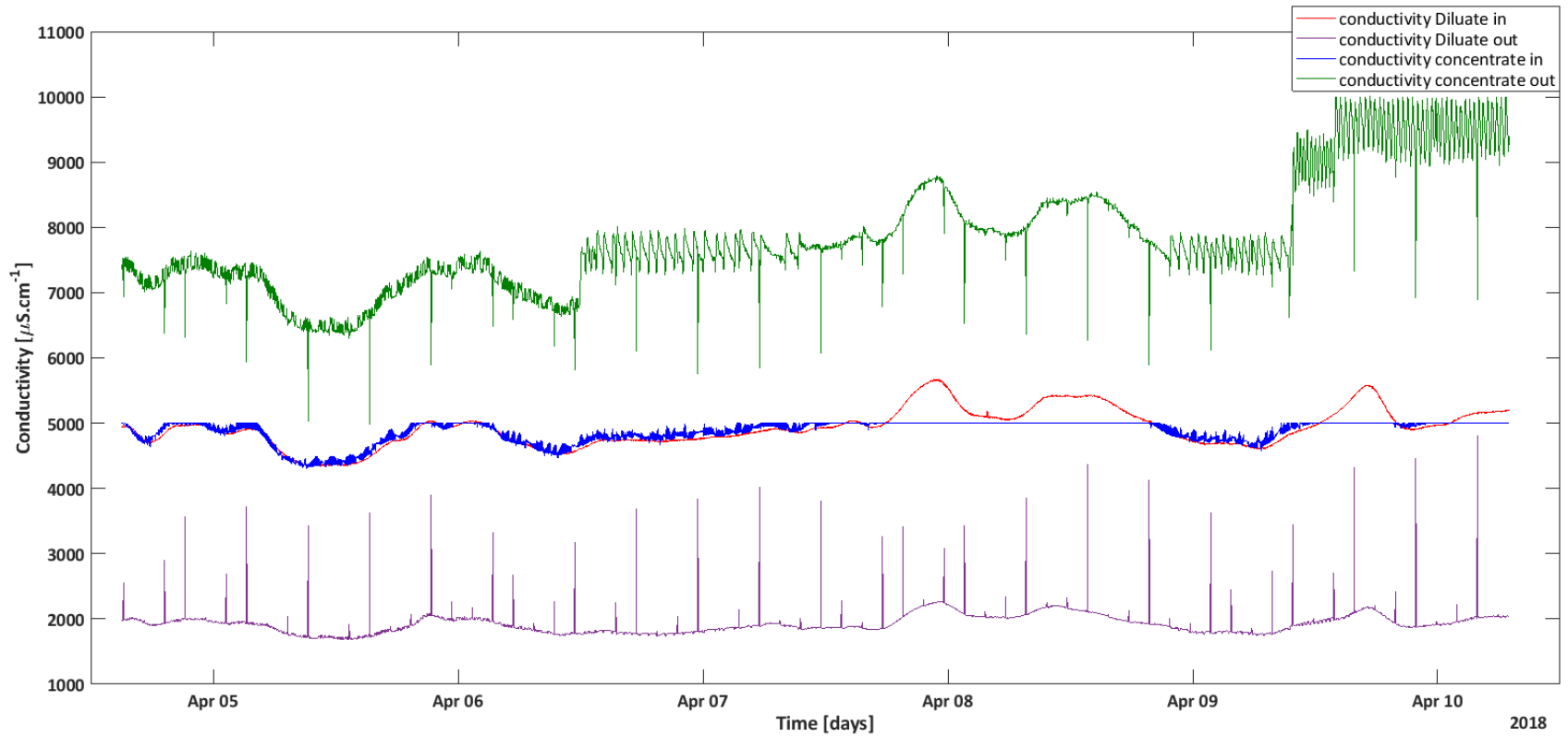


Figure 15. Conductivity of diluate in and out and concentrate in and out during Continuous mode.

Table 10. Analysis of the diluate stream during Feed and Bleed mode and Continuous mode

Setting	Diluate in						Diluate out					
	Conductivity (µS/cm)	NH ₃ (mg/L)	MDEA (mg/L)	Piperazine (mg/L)	MeOH (mg/L)	EtOH (mg/L)	Conductivity (µS/cm)	NH ₃ (mg/L)	MDEA (mg/L)	Piperazine (mg/L)	MeOH (mg/L)	EtOH (mg/L)
product quality (µS/cm)	Feed and bleed mode											
400	1492	383	13	<1	775	20	495	75	2.7	<1	1115	26
200	791	145	2.7	<1	713	22	202.7	45	2	<1	775	24
100	508	103	2.7	<1	107	3	98.9	31.1	1.9	<1	863	28
50	346	120	<1	<1	1282	27	56.6	13	<1	<1	1129	24
25	249	65	5	<1	1061	18	29.3	10	<1	<1	1193	21
maximum concentrate (µS/cm)	Continuous mode											
5000	4598	980	9	<1	1245	27	1775	475	12	<1	910	20
7500	4826	1725	8	<1	1405	28	1839	735	8	<1	1370	27
9500	5750	1527	29	<1	1247	22	2285	695	21	<1	1418	25

Table 10 shows the lab analysis of diluate in and out during both modes. During Feed and Bleed, methanol and ethanol passed through the stack and there was no significant removal while MDEA was partially removed by EDR. The fact that the primary alcohols are not removed is due to their neutrality, as EDR is mainly used to remove charged components. The same results hold for the Continuous mode, however the removal of MDEA was not sufficient in this mode which can be due to the single pass through the stack, but also to the higher incoming concentrations. On average, about 79% and 55% of the ammonia is removed in Feed and Bleed and Continuous mode, respectively.

4.2.2. Reverse osmosis

Fout! Verwijzingsbron niet gevonden.6 shows the permeate flux and recovery over time of these experiments. The vertical lines show where the recovery was changed. The high conductivity in the stream was due to a change in the production plant (on February 22nd 2018), which contributed to the ammonia content.

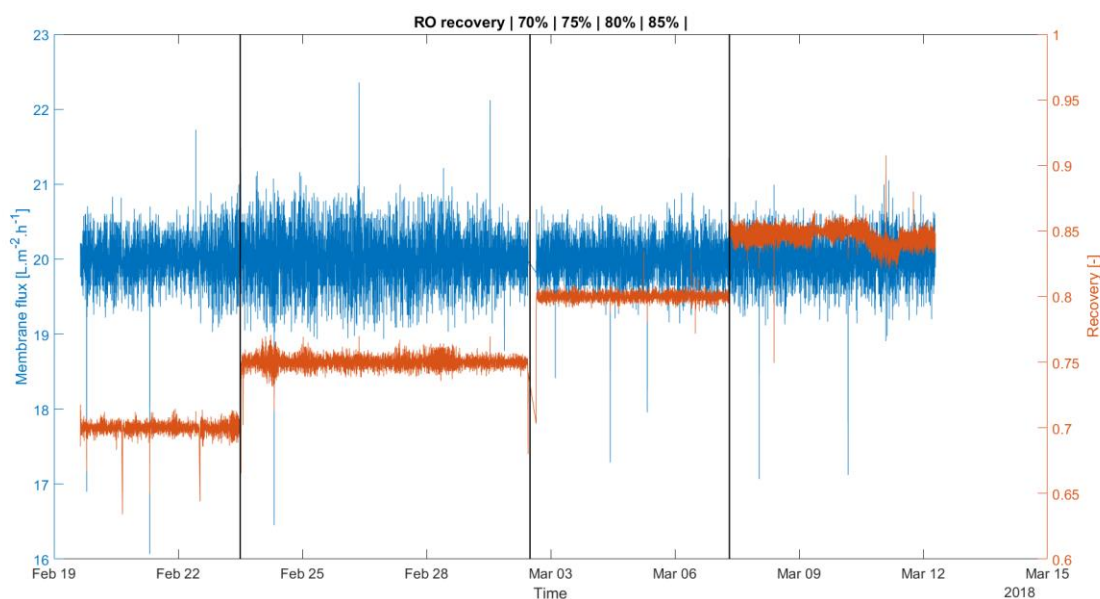


Figure 16. Membrane flux and recovery for the RO system.

Figure 17 suggests a correlation between permeate conductivity and the pH of the feed, while there is no significant correlation with the conductivity of the feed. The high conductivity of the permeate might be caused by H^+ -ions (protons) and therefore a correlation with pH can be suggested. However, at pH 6 there are large amounts of ammonium and CO_2 present in the feed and very few protons. Therefore, it can be concluded that the increase in permeate conductivity is caused by the relevant ions in the solution and not by the protons H^+ . Therefore, the conductivity is a measure for the amount of ions, rather than an indication of pH, in contrast to the effects seen for the C1 stream.

Figure 18 and **19** show the measured conductivity and calculated conductivity based on NH_3/NH_4^+ equilibrium and OH^- (thus pH) for feed and permeate, respectively. The calculated and measured conductivity show a high correlation, especially for the feed. The stream is saturated with CO_2 but the pH is rather neutral due to the presence of ammonia. So a correction of the conductivity for the presence of CO_2 nor NH_3 (1%) nor pH is essential for the C2 stream.

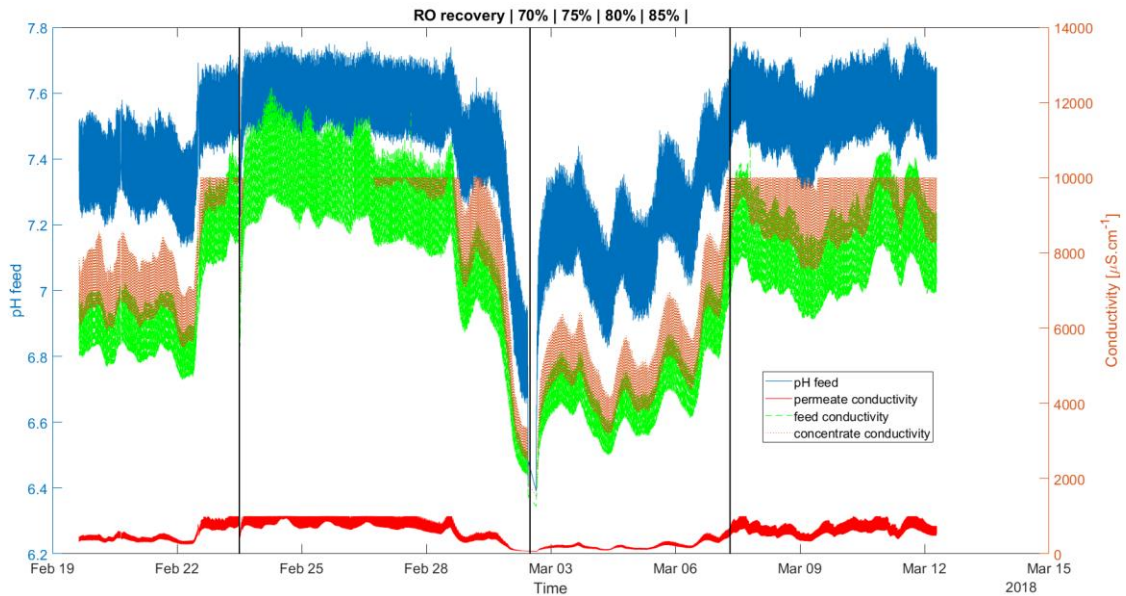


Figure 17. The pH of the feed and conductivities of feed, permeate and concentrate at different recoveries of 70, 75, 80, and 85% during RO treatment.

The highest possible value for the permeate conductivity was 10000 $\mu\text{S}/\text{cm}$ due to the range of measurement of the conductivity probe. This explains the unexpected behaviour of the permeate conductivity at higher values (as a flat line in **Figure 17**).

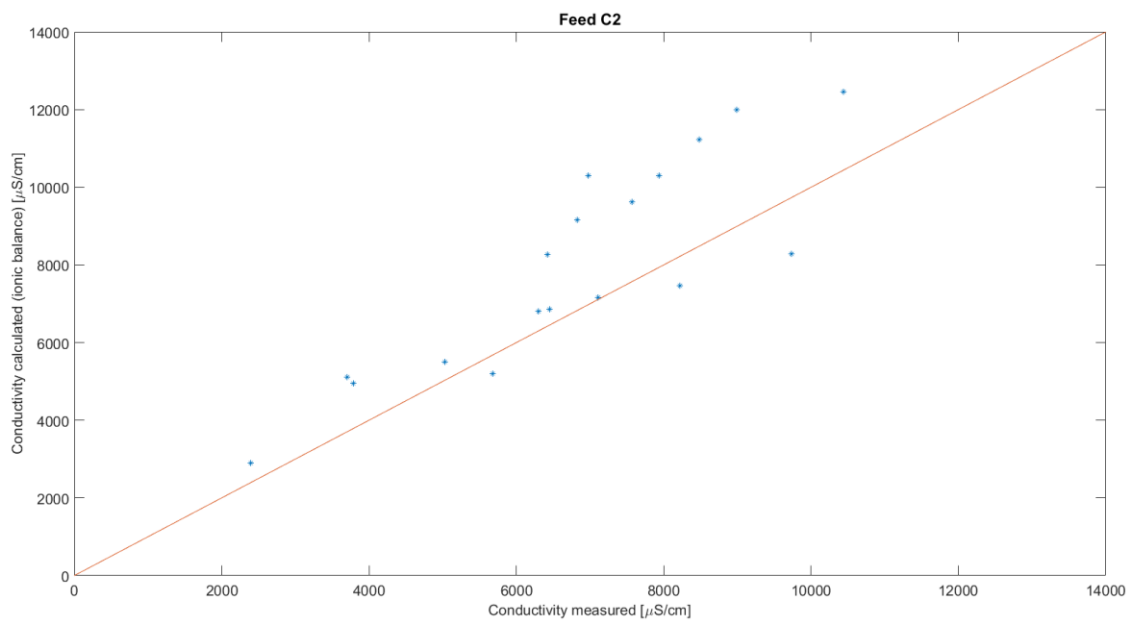


Figure 18. Measured conductivity and calculated conductivity (ionic balance based) for the feed of the C2 stream.

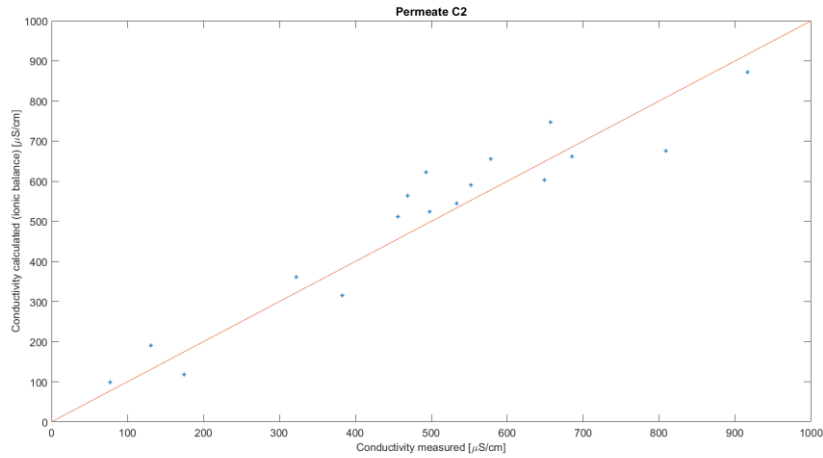


Figure 19. Measured conductivity and calculated conductivity (ionic balance based) for the permeate of the C2 stream.

Figure 20 shows the MTC of water through the RO membrane. This is an indicator for mass (transport) related to membrane fouling, while nominal salt passage is only recovery related. A drastic drop on the 22nd of February can be seen which is due to a change in the production plant. There is another jump on the 1st of March. In **Figure 21**, salt passage decreased while the MTC increased, which is due to the inverse relationship between these two parameters. Lower MTC indicates an increase in membrane fouling at higher recoveries.

A pH correction for the conductivities of feed and permeate is neglected as it had no influence. However, in surface water treatment MTC is most of the time decreasing, so here the sudden increment in March indicated a drastic change in the feed quality. In this case, the change (increase) in the conductivity of the feed is the main cause for the increase in the MTC. Another discussion point is related to the influence of temperature change in the plant on MTC and SP. For this reason, MTC and salt passage have been corrected for temperature, osmotic pressure and recovery.

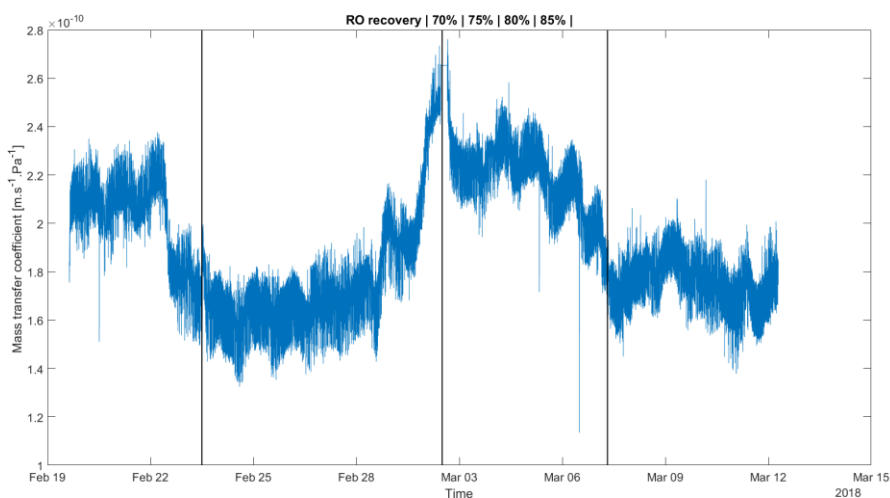


Figure 20. Mass transfer coefficient at different recoveries of 70, 75, 80, and 85% during RO treatment.

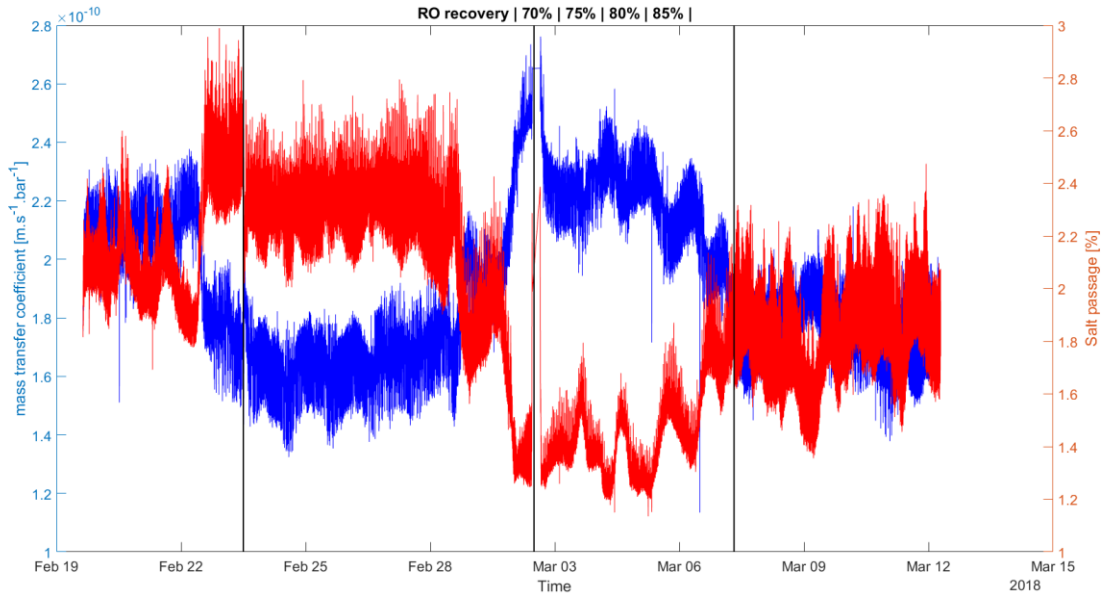


Figure 21. Mass transfer coefficient and salt passage at different recoveries of 70, 75, 80, and 85% during RO treatment.

Figure 22 shows that at higher recoveries, the nominal pressure drop is increasing. The slight increase in pressure drop indicated that at higher recoveries the membrane started to foul gradually. In these experiments nothing to prevent fouling, such as air flush or relaxation, was operational. These results suggest that in order to run RO continuously, one of these steps should be considered.

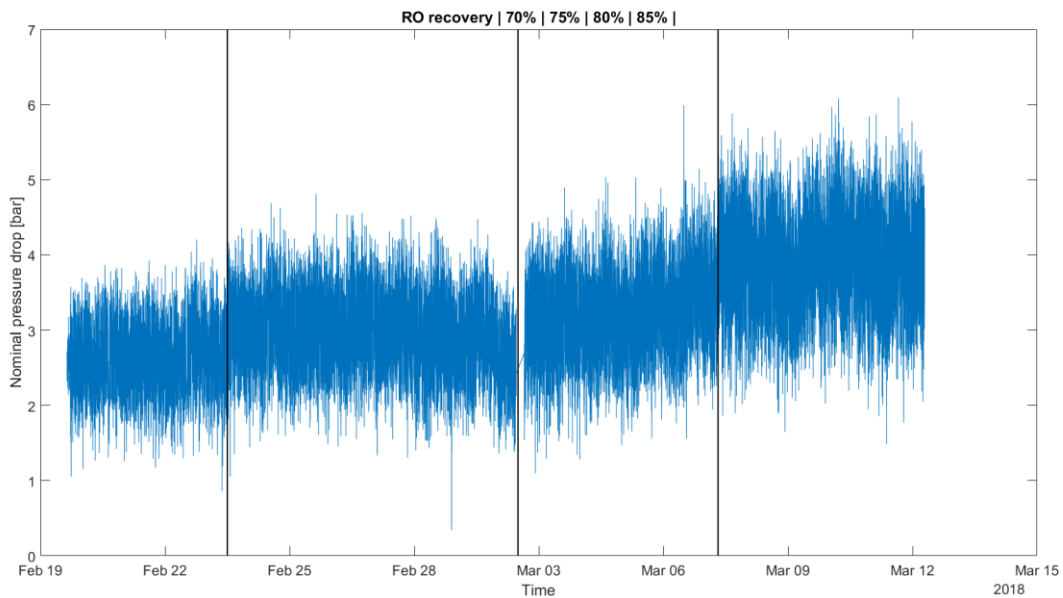


Figure 22. Nominal pressure drop at different recoveries of 70, 75, 80, and 85% during RO treatment.

Table 11. Lab analysis of feed and permeate at different recoveries during RO treatment.

Feed RO							Permeate RO						Removal (%)
Recovery (%)	Conductivity (µS/cm)	NH ₃ (ppm)	MDEA (ppm)	Piperazine (ppm)	MeOH (ppm)	EtOH (ppm)	Conductivity (µS/cm)	NH ₃ (ppm)	MDEA (ppm)	Piperazine (ppm)	MeOH (ppm)	EtOH (ppm)	
70	7109	1092	40	0,6	994	40	649	92	< 1	< 1	659	22	90
75	6971.9	1570	20	<1	677	28	493	95	<1	<1	677	22	92.9
80	6825	1398	17	<1	882	23	469	86	<1	<1	901	19	93
85	7570.2	1467	24	<1	959	30	552.2	90	<1	<1	989	20	92.7

Table 11 shows the lab analysis of feed and permeate at different recoveries. The removal efficiency based on conductivity at 70% recovery is for example 90% while at higher recoveries it is in the range of 93%. The removal of ammonia ranged between 92 and 94%. These are higher values compared to EDR. MDEA is completely retained, however, the major amount of methanol and ethanol passed through the membrane due to their small molecular size. The calculated specific electrical energy requirement for RO was 0.6 kWh/m³.

4.2.3. Membrane stripping

During a preliminary test, the performance of MS was investigated at a feed temperature of 55°C and a permeate temperature of 35°C. The results are given in **Table 12**. The ammonia flux is around 30 mg/m²/h, but lab-scale experiments showed that even higher fluxes can be reached, up to 30 g/m²/h.

The high conductivity in the stream is due to addition of salt and base and the probes in the installation are not designed to work with conductivities higher than 10000 µS/cm. Therefore, the conductivity measurements in the pilot were out of range for and are not presented here. The main observation is that there was no transport of MDEA. The pilot-scale experiments showed the passage of ammonia through the membrane towards the permeate side. There is a pH drop due to the dosing of acid in the permeate in order to convert the ammonia directly into ammonium and to keep it at the permeate side. Methanol and ethanol passed through the membrane due to lower boiling points of around 70°C while for MEDA is 247°C.

Table 12. Lab analysis of feed and permeate stream for the MS module.

		Feed							Permeate						
date	time	pH	T	Conductivity (μS/cm)	NH ₃	MDEA	MeOH	EtOH	Conductivity (μS/cm)	T	pH	NH ₃	MDEA	MeOH	EtOH
26/03	13:30	10.1	39.9	8410	122	79.0	880	17	9915	40	3.8	1228	< 1	795	16
	16:30	10.1	40.1	9410	18	9	569	12	9260	40	3.4	1273	< 1	818	18
27/03	13:00	10.0	39.8	9005	9	16	1307	27	17680	40	3.6	2108	< 1	720	18
	15:00	10	40.0	9410	5	17	909	18	19200	40	3.6	2076	< 1	966	16
28/03	9:05	10	39.8	8340	1	12	1058	21	24000	40.2	3.6	5730	< 1	1075	23
	13:55	10	39.8	6890	5	21	1004	20	22800	40.2	4.0	3151	< 1	1499	28
	15:50	10	40	7250	4	16	992	21	25100	40.2	4.0	3281	< 1	955	20
04/04	10:30	10.96	50.1	8760	3	9	1040	18	16980	50.3	3.97	2010	< 1	1415	26
	13:00	11	50	7640	3	7	1040	19	16810	50.2	4.12	2460	< 1	1095	20
	15:00	9.6	49.8	6380	1	12	1235	23	18320	50.1	3.56	2610	< 1	1070	18
05/04	12:20	10	50	8400	3	9	1030	20	25000	50.7	3.4	3280	< 1	1015	20
	14:20	10	50.1	8800	4	9	1180	24	28000	50.7	2.8	3550	< 1	1190	24
	16:20	10.1	49.6	8480	2	14	955	19	28600	50.1	3.1	3420	< 1	1035	21

In addition, the C2 stream was treated with ion exchange resins at lab-scale, the detailed information can be found in the respective document [6]. As a conclusion, the IEX set-up with a cation resin made it possible to remove the primary alcohols from the bulk stream, as ammonium and MDEA were retained by the cation resin. During regeneration these components can be recovered in a bulk solution. In a subsequent treatment with membrane stripping the MDEA can be separated from ammonia, as the results in **Table 12** suggest. Ammonia can be concentrated to very high concentrations in the permeate, without contaminants if IEX is applied first. MS is a promising technique concerning ammonia recovery.

4.2.4. Economic evaluation of the CO₂-condensate stream

For each technology the cost for maintenance was assumed to be 6% 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 economic analysis for EDR was based on a quote from 2013 taking into account a total inflation of 8% until the year 2017. The EDR membranes were expected to have a life-time of 10 years, whereas for the electrodes this is only 3 years. The economic analysis for RO was based on the knowledge of *Evides Industriewater*. Here, the average and maximum flow rate were set at 5 and 10 m³/h.

Table 13. Cost estimation for treatment of the CO₂-condensate stream by EDR.

OpEx	Amount	Price	Costs/year
Energy	657 000 kWh/year	€ 0.07/kWh	€ 45.990,00
HCl			€ 329,96
NH ₄ Cl			€ 5.329,00
Maintenance			€ 13.305,47
Membrane and electrode replacement			€ 55.020,63
Total			€ 119.975,06
CapEx	Amount	Price	Costs
ED membranes and electrodes	7	€ 72 554.68/stack	€ 145.109,36
Stack accessoires			€ 12.000,00
Pumps			€ 10.000,00
Electric supply			€ 20.000,00
Chemical storage and dosing	2	€ 8000/unit	€ 10.000,00
CIP tank & pomp			€ 5.000,00
Buffers			€ 8.000,00
Piping and valves			€ 6.000,00
Instrumentation			€ 10.000,00
Civil			€ 10.000,00
Process automation			€ 30.000,00
Total			€ 266.109,36

Table 14. Cost estimation for treatment of the the CO₂-condensate stream by RO.

OpEx	Amount	Price	Costs/year
Energy	40 764 kWh/year	€ 0.07/kWh	€ 2.853,47
HCl			€ 15,44
NaOH			€ 25,03
Maintenance			€ 5.856,00
Module replacement			€ 960,00
Total			€ 9.709,94
CapEx	Amount	Price	Costs
RO modules		€ 600	€ 4.800,00
Pressure vessels	10	€ 600/piece	€ 1.800,00
HP pump			€ 12.000,00
Chemical storage and dosing	2	€ 5000/unit	€ 10.000,00
CIP tank & pomp			€ 5.000,00
Buffer			€ 8.000,00
Piping and valves			€ 6.000,00
Electrics and instrumentation			€ 10.000,00
Civil			€ 10.000,00
Process automation			€ 30.000,00
Total			€ 97.600,00

The economic analysis for MD was based on a recent quote from Aquastill (23/08/2018).

Table 15. Cost estimation for treatment of the CO₂-condensate stream by MS.

OpEx	Amount	Price	Costs/year
Electric energy	125 201 kWh/year	€ 0.07/kWh	€ 5.680
HCl			€ 200
NaOH			€ 200
Maintenance			€ 19.374
Membrane replacement			€ 38.695
Total			€ 64.148
CapEx	Amount	Price	Costs
MD membranes	77	€ 2500/module	€ 193.474
Skid accessoires			€ 20.000
Pumps			€ 5.000
Electric supply			€ 50.000
Heating and cooling equipment			€ 40.000
Chemical storage and dosing	2	€ 5000/unit	€ 10.000
CIP tank & pump			€ 5.000
Buffer			€ 8.000
Piping and valves			€ 6.000
Instrumentation			€ 10.000
Civil			€ 10.000
Process automation			€ 30.000
Total			€ 387.474

The MD membranes were expected to have a life-time of 5 years. The source for heat recuperation was not included. Thermal energy needed for heating and cooling amounted 22 758 and 20 867 MWh/year, respectively.

For the economic evaluation the same remarks and conclusion can be drawn as for the SR800 stream. Both EDR and MS are too expensive compared to RO. For the production of boiler feed water, the best option is RO, based on product quality and production efficiency. However, the question is whether a switch from directly sending the stream to the wastewater to RO treatment is worthwhile if a mixed bed or another technology is still needed to meet the boiler feed water specifications.

When the main goal is to recycle the ammonia, MS is a valid option, not taking into account the high investment costs. Whether the investment is reasonable depends on the discharge costs of the condensate stream and the purchase costs for the new product component when no reuse is possible. If the cost-benefit evaluation is in favor of the reuse instead of the discharge, MS in combination with IEX is a very successful method to separate the ammonia from the other components and the bulk solution.

5. Conclusions

The selection of the most efficient technology depends highly on what is important for the client and what is the actual aim. So it can change according to the objective, for example in the YARA case for the SR800 stream, MD is suggested if the most important aim is the quality of the treated stream, as no additional post treatment step is required to meet the specifications for boiler feed water. Compared to EDR and RO, the product quality of the MD permeate was the best, as no ammonia or nitrate went through the membrane. However, this technique is very energy intensive and the flow rate of the product stream is very small. When water efficiency and economic aspects are taken into account, RO is the best alternative to the currently used IEX train.

Compared to the EDR treatment, the product quality obtained with RO is in the same range of the Continuous mode EDR experiments, except that the ammonia concentration in the RO permeate is much lower. In general, no decisive difference was observed concerning the product quality. The water efficiency for EDR was always higher than 85%, while this was not possible with the current pilot-scale RO set-up, due to the restrictions of the flow measurements. If these restrictions can be overcome, RO and EDR can show comparable results. Again it should be mentioned that the specifications for boiler feed water are not met solely with the RO treatment. An extra treatment technology after the RO module is therefore necessary, mainly to decrease the concentration of nitrate and to induce a further decrease in conductivity.

A last remark for the SR800 stream, there is a very important issue that should be taken into account for the evaluation of all the technologies studied in this project: the addition of HNO_3 . Whenever another treatment method could be used instead of ion exchange, a re-evaluation can be made on the necessity of HNO_3 addition. It might be possible that EDR, RO or MD needs less chemical addition, which can result in a decrease or elimination of the acid cost. Without the addition of HNO_3 , RO might give a better performance as less or no nitrate should be removed. During RO treatment the ammonium retention was very high compared to the nitrate retention (between 97-99% and 66-92%, respectively). In addition, the RO concentrate might be sent to the biological waste water treatment plant. This is not possible with the IEX treatment, as the waste water (coming from the regeneration) shows very high pH differences, due to the use of HCl and NaOH.

For the CO_2 -condensate stream the same conclusion can be made concerning the economic aspects without focusing on the product quality. During RO treatment MDEA is completely retained by the membrane, while NH_3 is retained for 92-94%, the primary alcohols end up in the permeate due to their neutrality and small molecular size. When the most important factor is the reuse of the ammonia, MS in combination with IEX gives the most promising results. During IEX, ammonia and MDEA can be separated from the primary alcohols as they will be adsorbed on the cation exchange resin. After regeneration, ammonia can be separated from MDEA by MS treatment due to a difference in vapor pressure.

Whenever a certain technology is chosen to be implemented in the future, a more in-depth economic evaluation is necessary to compare the new technology with the current one. In addition, the conclusions stated in this report are based on pilot-scale experiments ran over a limited amount of time. In order to investigate the performance of a new technology, a longer time-frame should be applied for testing stable operation of any specific technology.

6. References

- [1] E. De Meyer, M. Vanoppen, “Functional Description Electrodialysis Reversal”, pp.14, 2017.
- [2] H. Strathmann, “Electrodialysis, a mature technology with a multitude of new applications,” *Desalination*, vol. 264, no. 3, pp. 268–288, 2010.
- [3] A. Verliefde, “Functional Description Reverse Osmosis”, pp.16, 2016.
- [4] S. Derese, “Functional Description Membrane Destillation”, pp.15, 2016.
- [5] P. Van Elslande, “New technologies for ultrapure water production in the chemical industry: Case study at Yara”, Masterthesis at Ghent University, pp. 95, 2017.
- [6] B. Cousin, D. Overmeire, “SD7101 condensaat behandeling met IEX (opstroombehandeling)”, pp. 9, 2018.

7. Appendix

7.1. Condensate quality Yara Sluiskil B.V. (based on analysis from 2016)

Parameter	Unit		C1	C2
Discharge	m3/h	Average	46.4	5
		Max	68.4	
		Min	10.3	
Temperature	°C		40-50	38
NH ₄ ⁺	mg/l		73.5	277
NO ₃ ⁻	mg/l		71.4	-
Urea	mg/l		-	0.2
Fe	µg/l		1800	-
SiO ₂	µg/l		17	-
HCOO ⁻	mg/l		<0.2	-
Cl ⁻	mg/l		<0.1	<1
SO ₄ ²⁻	mg/l		<0.1	2.3
TOC	µg/l		2000	Saturated with CO ₂
Formol	mg/l		-	0.82
Methanol	mg/l		-	1128
Ethanol	mg/l		-	30
PO ₄ ³⁻	mg/l		<0.1	<1
Conductivity	µS/cm	Average	224	3518
		Max	2025	
		Min	40	
pH	-		9.2 [*]	6.8

* = Can strongly fluctuate

- = not measured

7.2. Used equations

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

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

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

Where U_{par} is the 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.

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

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

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

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

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

Where NPD is nominal pressure drop [kPa], Q_{feedn} nominal design feed flow of the RO system [$m^3 \cdot h^{-1}$], $Q_{concentraten}$ nominal 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.

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

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

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

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

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

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

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