Wetlands & hybrid desalination at Dow Terneuzen

Technical report of pilot study

April '19 – August '21

COLOFON

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SUMMARY

By 2024 Dow Benelux BV and Evides Industriewater will implement a facility that allows the reuse of almost 8 million m³ annually of a mix of waters from various sources. Water will be supplied from the Terneuzen municipal treatment plant, Dow's wastewater treatment facility, and rainwater collected from the Dow premises and its periphery. Dow Benelux BV and Evides Industriewater have partnered with the Water Authority Scheldestromen in conducting a two-year pilot-research, which consists of a constructed wetland (CW) as pretreatment followed by a brackish water line consisting of ultrafiltration (UF), softener (WAC), scavenger (SBA) and reverse osmosis (RO) for the removal of salt and organic substances to produce a high quality process water (<50 µS/cm).

Constructed wetlands as pretreatment for mild desalination

Results indicate that using aerated constructed wetlands for biological stabilization of industrial- and municipal effluent is a stable, reliable, energy-efficient and biodiversity enhancing pretreatment technology that enables reuse for mild desalination. No reference projects were found using CW's as a pretreatment for mild desalination. Therefore, the pilot had to be designed 'from scratch' and assumptions in operational performance varied highly. Over the course of two years, various analyses were performed testing the biological stability, standard nutritional parameters, salts & metals before and after the constructed wetland. After a start-up period of three months where sulphate-, silica- and iron-leaching from the substrate expanded clay aggregates was observed, the wetlands showed a stable treatment performance. Optimal operational settings regarding aeration, suspended solids loading, hydraulic retention time (12 hours) and carbon dosing (none) were found, giving a confident basis for the full-scale design and final operational performance. Apart from the effect on standard parameters, micropollutant removal in CW's was of special importance for the Water Authority Scheldestromen. Four sampling rounds were held, of which the last two were done according the guidelines form the Innovatie Programma MicroVerontreinigingen (IPMV) organized by STOWA. Results are promising for most components, ranging from 5-95% removal, depending on which component is looked at.

Mild desalination: ultrafiltration, softener, scavenger and reverse osmosis

Evides Industriewater does not yet operate a demineralization plant that is specifically designed to optimize the water recovery through UF, WAC, SBA and RO, reuses the RO-brine ánd uses domestic- & industrial effluent as feed. Therefore, assumptions were varying highly in the predesign. These assumptions have been proven or debunked, resulting in a more confident basis for the full-scale design & performance. For the UF, a filtration time of 60 minutes, flux of 60 lmh and chemically enhanced backwash frequency (CEB) of 24 hours provided a stable production process, as opposed to 40 minutes filtration time and 24 hours CEB-frequency in the predesign. This indicates less downtime, less energy use, less water loss and possibly less UF-membranes that need to be installed. For the SBA, the resin type, standard operational capacity and functional requirements were determined. This provided a basis for vessel dimensioning. The WAC is still under investigation in Q4 2021, but assumptions on this type of resin are considered less of a risk. For the RO, optimal cleaning strategies, operational settings and subsequent fouling behavior was determined. Some (partly) irreversible organic fouling was observed over all elements related to a component in the industrial effluent. As a result, cleaning of the RO-membranes should be done once every two weeks, as opposed to once every 4 weeks according to the predesign. No biological fouling was observed on the elements.

Brine reuse for optimal water recovery in mild desalination

The results indicate that reuse of RO-brine for backwashing the UF has no negative effect on performance and can be safely and reliably implemented in the full-scale design. Reuse of RO-brine as regeneration water for SCAV has also proven possible, thus increasing recovery of the whole treatment line by 5-10%. Some operational specialties, such as rinsing the membranes after backwash, have been noted in the report.

Overall, the complete treatment train is considered a technically viable option for providing high quality process water for Dow Terneuzen from local (brackish) sources. The pilot-research has given significant insights in the design, operation and risks related to this innovative treatment concept for a demineralized water plant.

1. INTRODUCTION

1.1 Background

By 2024 Dow Benelux BV and Evides Industriewater will implement a facility that allows the reuse of almost 8 million m³ annually of a mix of waters from various sources. Water will be supplied from the Terneuzen municipal treatment plant, Dow's wastewater treatment facility, and rainwater collected from the Dow premises and its periphery. Dow Benelux BV and Evides Industriewater have partnered with the Water Authority Scheldestromen in conducting a pilot-research, which consists of a constructed wetland as pretreatment followed by a brackish water line for the removal of salt and organic substances to produce a high quality process water (Figure 1).

This report summarizes the results of the two year pilot research, held from April ’19 to August ’21 and **focuses on the technical aspects**.

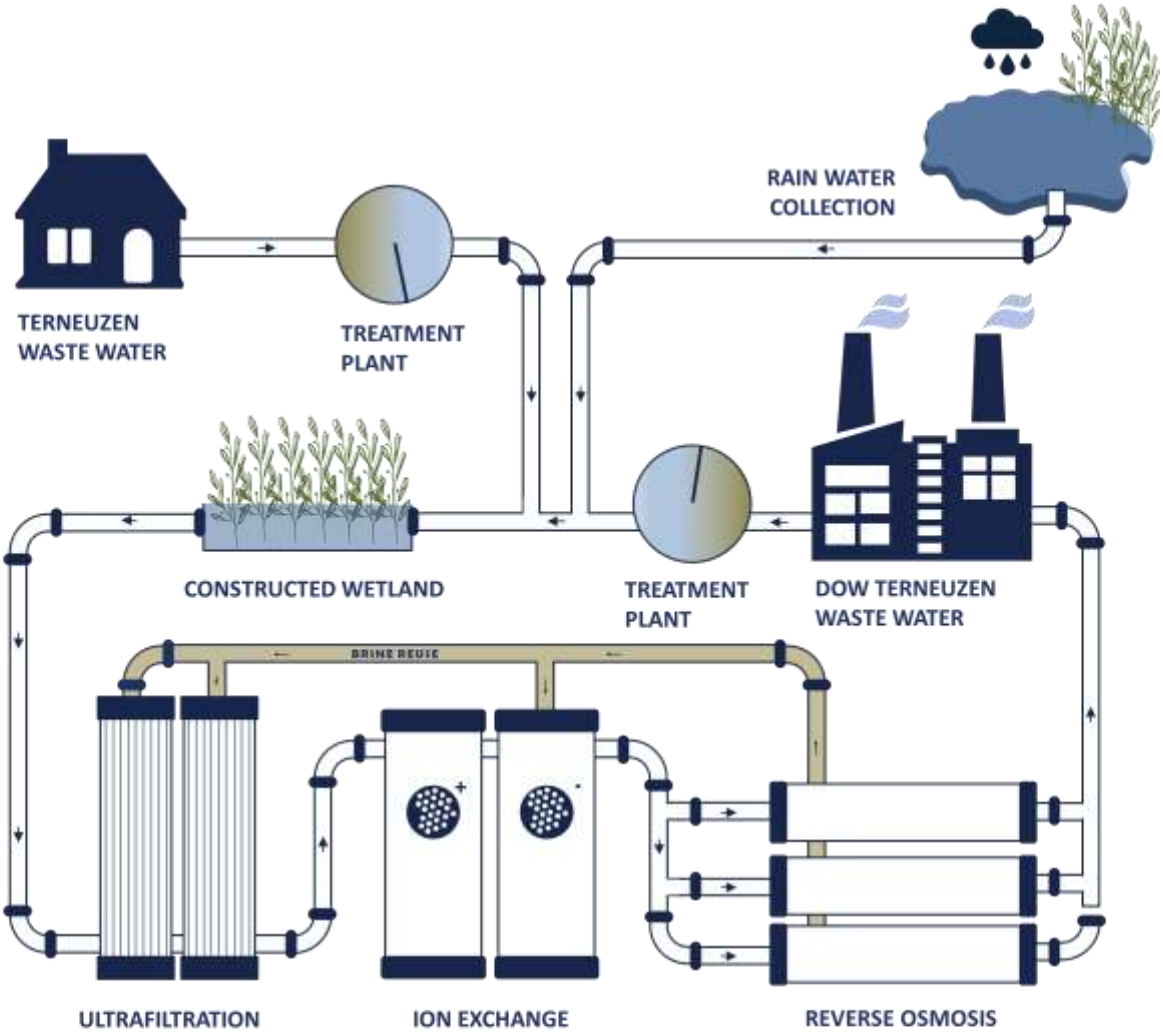

Figure 1: Overview of the full scale technology plan.

1.2 Goals & research questions

The main goals of the Joint Development Project are to:

- determine the feasibility of reuse of industrial and domestic wastewater as sources for industry by combining 'green' infrastructure (wetlands) and novel technological concepts (hybrid desalination).
- determine the techno-economic feasibility of wetlands as a pretreatment step for mild desalination (Dow-Evides).
- determine the feasibility of using wetlands to remove micropollutants from effluent to enhance surface water quality.

To reach these goals, the research questions below have to be answered. This report summarizes the technical input needed to determine the technical feasibility of the Flagship Scenario[1] as compared to the Base Case scenario[2].

Water mass balance

Which water losses can be identified related to evaporation in the wetlands?

Which water additions can be identified due to rainfall on the wetlands?

Which water (and how much and for how long) needs to be used to start up the wetlands?

Wetland

What is the optimal design for a full-scale wetland as pretreatment for hybrid desalination?

What is the seasonal effect on treatment performance?

What is the effect of separate or mixed feed flows (domestic and/or industrial)?

How to operate the wetland?

Which waste streams are coming from the wetland (reed, biomass, clay)?

What is the effect of wetlands on micropollutant-removal on industrial and/or domestic effluent?

Which are the characteristics of the wetland substrate before and after use?

Hybrid desalination (UF-WAC-SBA-RO)

Which effect does pretreated water have on the organic fouling of RO?

Which design & operational parameters need to be taken into account for the UF?

Which design & operational parameters need to be taken into account for the WAC-SBA?

Which design & operational parameters need to be taken into account for the RO?

Which effect does using RO-concentrate for backwash and regeneration have on:

- operational parameters of the UF?
- operational parameters of the softener-scavenger?

Feedwater characteristics

What characteristics does the industrial effluent have, how does this affect the treatment line and how will this change during the contract?

What characteristics does the domestic effluent have, how does this affect the treatment line and how will this change during the contract?

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[1] Flagship scenario – constructed wetlands as pretreatment.

[2] Base case scenario – double layer filtration & biologically activated carbon filtration as pretreatment.

1.3 Reading guide

Chapter 2 (Methodology) discusses the setup and execution of the research. The main research aspects and the choice of the treatment concept are explained here. Each pilot (wetland, UF, WAC-SBA and RO) has its own subchapter, even though a lot of overlap exists between experimental setups. In chapter 3 the results are summarized and discussed. Finally, chapter 4 gives recommendations on the design parameters that can be used in designing the full scale plant.

Due to the intertwined character of the treatment setup (for example, every change in settings for the wetlands affects the product water quality and therefore the performance of subsequent pilots), the split has been made per pilot. In every experiment, the context (e.g. feedwater quality, other changing parameters that influence results) is explained.

Research is ongoing until the end of 2021. Results from this research are mainly considered as optimizations that do not have a significant impact on the treatment concept.

2. METHODOLOGY

2.1 Pilot setup

The pilot is fed with two main flows. One flow (effluent from the WWTP Terneuzen) is coming from the existing Membrane BioReactor (MBR), including the dosage of monochloramine (MCA). This free chlorine is neutralized onsite with sodium bisulfite and extra ammoniumchloride is dosed to simulate the expected concentrations in the full scale effluent of the WWTP Terneuzen. The second flow is coming from the sweet WWTP of the Dow-site, called Biox. Both streams can be controlled to achieve the desired mix. The collected rainwater, which will be part of the full scale design, is not part of the trial as previous research (www.E4Water.eu) revealed that this water source hardly requires any pretreatment prior to the mild desalination step.

After pretreatment in the constructed wetlands, the water flows through the ultrafiltration (UF), softener, scavenger (IX) and finally the reverse osmosis unit (RO). The concentrate of the reverse osmosis unit can then be used for regenerating the scavenger resin or backwashing the ultrafiltration (Figure 2).

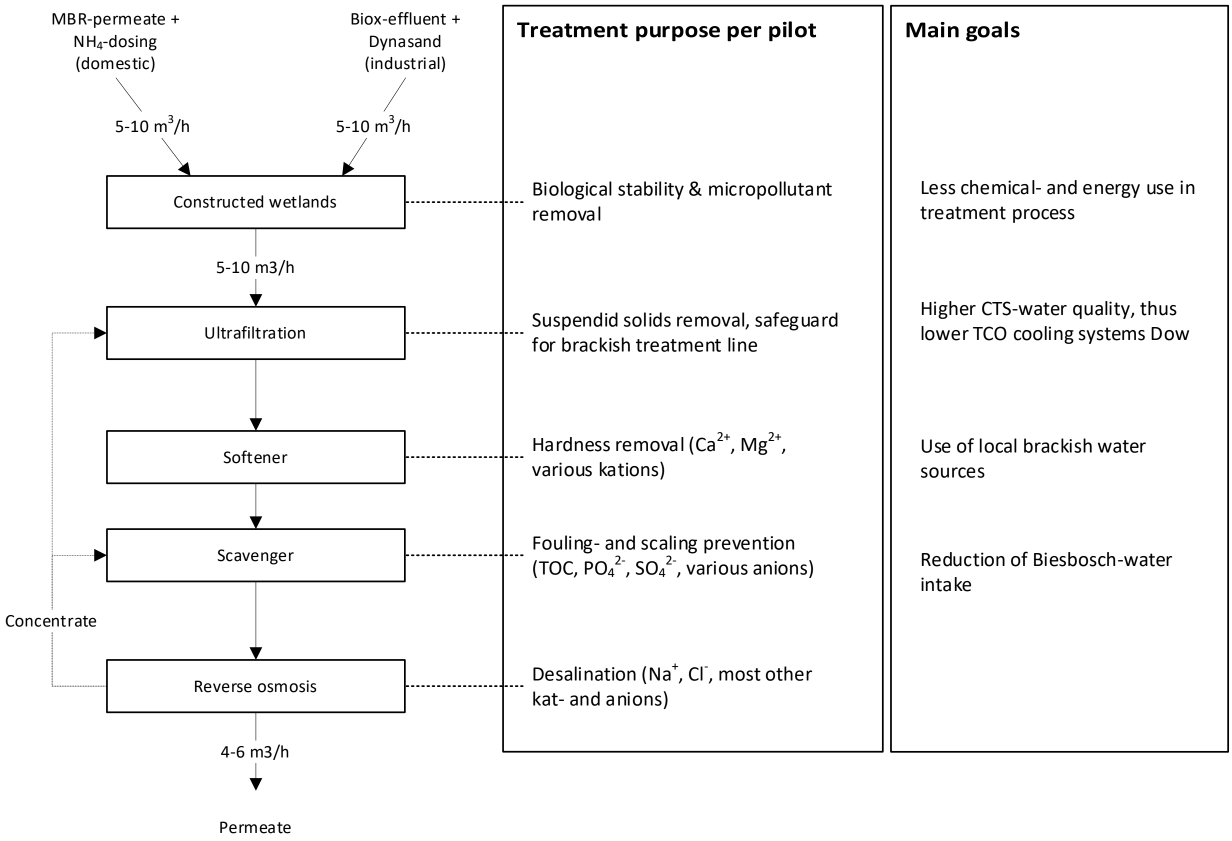

Figure 2: Overview of pilot setup, treatment purpose per step and overall goals of the project.

Attachment B states the quality requirements as mentioned in the WSSA. Actual measurements are used for the experiments. Discrepancies between assumed water quality and actual water quality are addressed in each experiment. The main differences between pilot and full scale are:

a. There is no Spuikom water being fed to the pilot. The expected impact on research results of not having Spuikom water is expected to be minimal. Water provided by Spuikom in full scale is low (7% of total volume) and the quality does not induce any suspicions for causing problems later on.

b. MBR-permeate is used for simulating WWTP Terneuzen effluent. The major differences between pilot and full scale for this feedflow are:

- Ammonium dosing for full scale simulation. The pilot MBR-feed will always have ~2 mg/l NH_4-N added to the flow to simulate the expected full scale concentrations.
- Total Suspended Solids. The pilot receives water with low turbidity (0-2 mg/l TSS) compared to the full scale case (10-20 mg/l TSS). As there is no practical way to simulate the TSS, this bias needs to be taken into account when interpreting the results.

2.2 Main research aspects

In 2017 the first pre-liminary design calculations were made for the beforementioned treatment concept. This rough schematic was used to determine the advantages of the overall concept. At that stage the proof of concept was not there and the design was based on rough estimations. A proof of concept at pilot scale was needed and research at this scale was essential to make a proper design with acceptable inaccuracies.

2.2.1 Wetlands

In this treatment concept, aerated horizontal flow constructed wetlands are used to stabilize the effluent from the domestic and municipal WWTP's. Overall, the wetlands are expected to enhance water quality towards the UF, IX and RO by reducing ammonium, suspended solids, organic carbon and nitrate. The concept works with an actively aerated reactor[3] filled with expanded-clay granules, on which a biofilm grows. Reed is planted on top, but not considered essential for enhancing water quality. Harmful components are either degraded by the bacteria or accumulate in the wetland. Nitrification occurs in the aerated zones, denitrification in the non-aerated zones, provided there is sufficient carbon source.

Key in this concept is the claim that it is an environmentally friendly, cost-effective, and easy to be maintained way to stabilize domestic and industrial effluent, compared to double layer filtration followed by a biologically activated carbon filter.

2.2.2 Ultrafiltration

In this treatment concept UF-membranes are used as a pre-treatment for the IX and the RO. The purpose of the UF is to remove turbidity / suspended solids from the water stream and to act as a safeguard for the subsequent ion-exchange unit. Ultrafiltration is often applied as a pre-treatment for desalination processes. The main research aspects can be split into two:

- Performance with- or without CW as a pretreatment step
- Performance with- or without using RO-concentrate for backwashing.

2.2.3 Ion exchange – softener and scavenger

The full-scale design of the IX unit consists of a softener and a scavenger IX columns in series. The concept behind the full-scale design is that the softener unit can remove cations such as Ca^{2+} and Mg^{2+} (water's hardness) and the scavenger unit can remove nutrients that can cause biofouling such as NO_3^-, HPO_4^{2-}-P[4]and TOC as well as ions that can cause scaling such as SO_4^{2-}. This way, the feed of the RO unit will have lower biofouling and scaling potential with consequently lower operating costs (lower chemical use, less frequent replacement of membranes). TOC removal in RO feed can also reduce the potential of membrane irreversible fouling.

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[3] Patented PhytoAir-system.

[4] PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$ species of phosphate will be referred as HPO_4^{2-}-P and expressed in mg P/L in this report, since HPO_4^{2-} is the dominant species based on water's pH.

For the softener a WAC resin (Amberlite MAC-3 H) was chosen, while for the scavenger a SBA resin (Amberlite 958 Cl) was chosen. The IX unit was designed to consist of 7 lines, from which 6 would be in parallel production and 1 in regeneration with a gross flow 171 m^3/h. The softener was designed in order to remove calcium (Ca^{2+}) and magnesium (Mg^{2+}) from the feed water. The scavenger was designed to remove sulfate (SO_4^{2-}) and total organic carbon (TOC). Moreover, some assumptions about the expected operational capacities (OC) for both resins were made. Specifically, for the WAC it was assumed that the OC would be equal to 100% of the total resin's volume capacity (TVC) [5] and for the SBA it was assumed that the OC would be equal to 90% of the TVC (safety factor of 10%). The resulted resins volumes for both the WAC and the SBA resin are given in Table 1.

Table 1: Full scale design resins, assumed operational capacity and resulted resin volumes

Resin Type	**WAC**	**SBA**
Resin	Amberlite MAC-3 H	Amberlite 958 Cl
Feed water concentration (eq/m^3) - cations to be removed: Ca^{2+} and Mg^{2+} - anions to be removed: SO_4^{2-}	5.13	2.98
Required throughout/ batch (m^3)	4000	4000
Assumed OC (eq/L_R)	5.2 (H^+ form) 3.25 (Na^+ form)-60% swelling from H^+ to Na^+ form	0.8 (Cl^- form) 0.72 (Cl^- form) – 10% safety factor
Required resin volume (L)	3,946	16,553

The regeneration of the WAC was designed to take place in two main steps; (i) HCl dosing to replace the removed cations with H^+ ions and (ii) NaOH dosing to replace H^+ ions with Na^+ ions. The regeneration of the SBA was designed to take place with NaCl to replace the removed anions with Cl^- ions. Moreover, the dosing of the NaOH and NaCl was intended to be combined by using a mixed solution of both chemical through both the WAC and SBA columns in series. With the initial compaction, two displacement steps, rest and prewash the regeneration steps for the WAC resin were designed to be 8 as described in Table 2. Steps 2 and 3 were designed to take place only to the WAC resin columns, while the first and the last 4 steps were designed to be combined with the regeneration of the SBA resin columns. In Table 3 the regeneration steps of the SBA resin are given. Step 1 which was an initial rinse was supposed to take place with step 1 of the WAC resin regeneration. Then, step 2 should be performed with step 4 of the WAC regeneration, step 3 with steps 5 till 7 of the WAC regeneration and finally step 4 with step 8 of the WAC regeneration. This simultaneously regeneration of both WAC and SBA columns would results in a total regeneration duration of 3.7 h.

Brine reuse was considered as a valid option for the regeneration of both resins. By the term brine reuse in IX operation is meant the application of the follow up RO's concentrate waste stream for regeneration purposes. The idea was that the RO concentrate will consist mostly of Na^+ and Cl^- ions, which are valuable for the regeneration of the WAC and SBA resins, respectively. As it can be seen in the tables below, 8 out of the 11 regeneration steps were designed to take place with RO concentrate. Subsequently, low amounts of demineralized and/or IX product water would be required for regeneration purposes that resulted in a recovery of 98% for the IX softener-scavenger system. Finally, the required consumptions of chemicals for the regeneration are given in Table 4 and Table 5.

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[5] Please note that the TVC of MAC-3H based on the current available datasheet is 3.8 eq/Lr (10; 3). However, when the design was made the known TVC for this resin was 5.3 eq/Lr and this value was used for the full scale design.

Table 2: Regeneration steps WAC

Step	Direction	Water source	Velocity (m/h)	Flow (BVh)	Volume (BVs)	Duration (min)
1. Compaction	Upflow	RO concentrate	25	21.0	0.89	3.6
2. Regeneration with 6% HCl	Downflow	Demin water	4.5	6.0	2.74	44
3. Displacement	Downflow	RO concentrate	4.5	6.0	1.25	20
4. Regeneration with 2.2% NaOH	Upflow	RO concentrate	8.0	10.8	8.77	78
5. Displacement	Upflow	RO concentrate	8.0	10.8	4.5	25
6. Settling/bed rest	-	-	-	-	-	10
7. Displacement	Downflow	RO concentrate	8.0	10.8	4.5	25
8. Prewash	Downflow	Product water (other lines)	8.0	10.8	3.6	20

Table 3: Regeneration steps SBA

Step	Direction	Water source	Velocity (m/h)	Flow (BVh)	Volume (BVs)	Duration (min)
1. Rinse	Downflow	Concentrate from WAC step 1	6.0	3	1	20
2. Regeneration with 2.9% NaCl	Downflow	RO concentrate	5.3	2.6	3.34	78
3. Displacement	Downflow	Concentrate from WAC steps 5&7	5.3	2.6	3.00	70
4. Prewash	Downflow	Product water (other lines)	5.3	2.6	0.9	20

Table 4: Chemical consumptions – WAC regeneration

Chemical	HCl	NaOH
Stoichiometry (%)	105	105
Consumption (g/m^3 water produced)	196.4	215.4

Table 5: Chemical consumptions – SBA regeneration

Chemical	NaCl	
Option	Min	Max
Chemical dosage (g NaCl/ L_R)	60	80
Stoichiometry (%)	143	190
Consumption (g/m^3 water produced)	248.3	331

2.2.4 Reverse-osmosis

A standard design for the full-scale RO with a production capacity of 240 m³/h was made. A stable operation of the RO membrane process needs to be achieved based on the requirements listed in Table 6. The salt rejection needs to stay stable and the final product has to meet 40 µS/cm as an average and 50 µS/cm is the maximum allowed conductivity (CTS product, see Annex A).

Table 6: Assumed operational settings full-scale RO design

Parameter	Full-scale
Recovery	85%
Flux	20.6 LMH
Membranes	ECO PRO 400i
Staging	31x6 15x6 6x6
Salt passage	99.7%
Dosing	None

The aim is a yearly average operation with a fouling factor minimum of 0.8 and joint annual feed pressure of 14 bar (including 1 bar extra pressure drop over each array) at a yearly average temperature of 16 °C. Contamination needs to be reversible with a maximum CIP frequency of once a month for each array.

2.3 Choice of treatment concept & methodology

2.3.1 Wetlands

An aerated Horizontal Subsurface Flow (HSSF) constructed wetland was chosen as preferred design for Dow[6]. In an HSSF, the water is fed from horizontal pipe with openings at regular intervals to distribute the water equally over the inlet zone. The water flows horizontally through the filling material to the outlet zone where the treated water is collected. The water level is kept below the surface of the filling material to reduce odor issues and evaporation of volatile constituents. By additional aeration the efficiency of the wetland can be improved. Aerated wetlands can treat the same load but with a 4 times lower footprint than non-aerated wetlands[7].

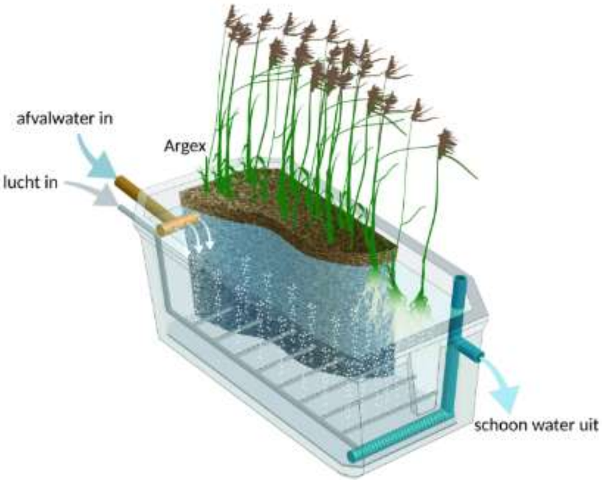

Figure 3: concept of HSSF Aerated Constructed Wetlands.

The pilot consists of two HSSF-CW (horizontal subsurface flow constructed wetlands) of 350 m² each (28m x 12.5m), which were each fed with 8-12 m³/h of either municipal effluent from WWTP Terneuzen, effluent Biox from Dow or a combination of both streams. Both wetlands cells are filled with LECA (Low Weight Expanded Clay Aggregates and can be aerated in three separate zones, by means of blowers, connected to aeration grids at the bottom of the wetland cells. All zones are equiped with an in-situ DO-sensor (Dissolved Oxygen), where the DO-results are used to control the oxygen levels in the different zones.

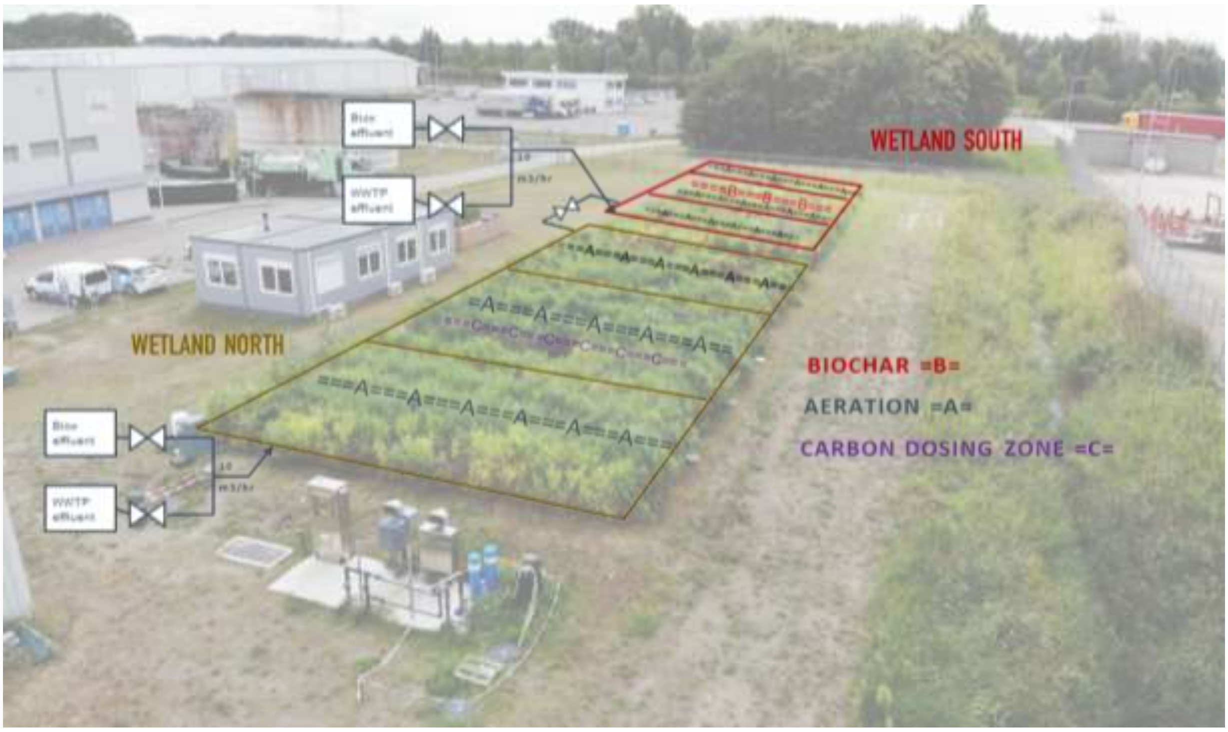

Figure 4: Overview of two Constructed wetland pilots at DeCo.

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[6] PHYTOAIR® – AERATED CONSTRUCTED WETLAND, Rietland BVBA

[7] Information provided by Rietland BVBA.

With an hydraulic load of 10 m^3/h, assuming a substrate porosity of 35%, the hydraulic retention time in each wetland cell is 12h. The water flows horizontally through the filter material, that is planted with Phragmites australis. One of the cells (Wetland North) has the possibility for controlled dosing of a highly concentrated easy degradable carbon source at the beginning of the second zone.The amount of carbon dosed is based on the in-situ nitrate measurement just before the C-dosing area and an emperically determined optimal C/N factor. The other cell (Wetland South) contains a zone where biochar was mixed with the LECA to enhance removal of emerging pollutants. The two wetlands can be operated in parallel mode or in serial mode where the latter will double the overall retention time. The influent to the wetlands can be either Biox or MBR or a mix of both streams. Besides the dissolved oxygen probes in the three zones of each wetland, ammonium and nitrate-N are monitored continuously.

At the end of the first zone of wetland North, a NITRATAX N-NO_x analyser is installed in a flow-through compartment with inlet and outlet screen (0-40cm below groundlevel).

Figure 5: Pilot location at Dow Terneuzen.

By a valve system on a manifold, the 4 streams (2 influents and 2 effluents) are alternately sampled and directed to analyser system consisting of an UV-based NX-7500 analyzer and an AMTAX N-NH3 analyzer in series. The NX-7500 analyzer is an UV-based monitoring probe reporting N-NO_x, TSS, SAK254 and COD. Only the N-NO_x data gave reliable results. After passing the NX-7500 probe, the sample stream is sent to an AMTAX NH_3-N analyzer. Initially grabsamples were taken on workdays for various analyses, where Tuesday sampling and analyses was performed by AQUALAB and Wednesday sampling and analyses was performed by the Dow lab. On Monday, Thursday and Friday the wetland samples were analysed at the DeCo plant by the operators/interns. End of 2020 autosamplers were installed on the inlet- and outlet of both wetlands for micropollutant sampling, but later on also for the regular monitoring over the week.

During the research period many operational parameters have been investigated where following are important for the final design:

- Aearation settings
- Hydraulic loading
- Temperature/seasonal effect
- Use of Biochar
- Dosing of an additional Carbon Source to enhance denitrification
- Hydraulic load/mass load effect on performance

The following indicators/parameters were used to evaluate the effect of the different modes of operation:
- COD, N-NH_3, N-NO_3, O-PO_4, SO_4, Total Suspended Solids (TSS)

Additional sampling has been performed to gather knowledge on:
- Biological activity on Argex samples by the University of Ghent
- Biological activitiy of feedwater and treated water using the WLN-monitor and ATP-measurements
- Micropollutants removal in wetland and brackish water line
- AOX (adsorbable organic halogens) and *Legionella*

2.3.2 Ultrafiltration

The modules used for the research are the IntegraFlux™ SFD-2880XP modules from Dupont. The membranes are made from PVDF hollow fibers with a pore size of 0.03-µm, each membrane has a filtration surface of 77m^2. In the feedwater line of the membranes a bag filter is placed (200µm) to protect the system from large particles. The supplier recommends to operate the system within the limits indicated in Attachment C. The filtration occurs outside > in and is dead-end. The membranes can be cleaned by applying (air-enhanced) backwashes (BW, flush inside > out) and chemical enhanced backwashes (CEB) with UF product water. A cleaning in place (CIP) can be done if the BW's and CEB’s are not able to clean the membrane fully. The supplier's recommendations to clean the membranes are visible in Attachment C. The operational performance of the UF is dependent on the chosen settings and feed-water quality. The feed-water quality should be within the limits indicated in Table 7.

Table 7: Feedwater requirements for the UF modules.

Parameter	Unit	Design basis	Maximum allowable
Turbidity	**NTU**	**<50**	**300**
COD	**mg/L**	**<20**	**60**
TOC	mg/L	<10	40
TSS	mg/L	<50	100
Temperature	°C	25	40

Within this research the performance of the system is followed by keeping track of the permeability and pressures during filtration (and backwashes). A successful configuration will result in a stable permeability that doesn't change much over longer periods of time. The applied cleanings (BW and CEB) should be able to get the permeability back to its original state (close to clean membrane permeability). During filtration the permeability normally will drop as the membrane gets fouled (fouling of the membrane can happen at the membrane surface on the feed side, but also on the permeate side or inside the pores), the BW should be able to remove particles / cake layer from the membrane surface after a filtration period. CEB's will be applied periodically to remove fouling that cannot be removed by the backwashes and will contain chemicals that are dosed in the backwash stream:

- A combination of caustic soda (NaOH) and sodium hypochlorite (NaOCl) to remove organic and biological fouling.
- An acidic cleaning (citric acid or HCl) to remove scalants.

Within this research the effect of the constructed wetlands on the performance of the UF system was of the highest interest. In order to clean the UF system with BW and CEB, permeate of the UF is used as cleaning water. This means that there is a loss of treated water, as this permeate ends up in the waste stream. Another waste stream in this treatment concept is the brine of the RO, which could be used by performing the backwashes of the UF system with RO brine.

For the different scenarios assumptions were made for the full-scale design beforehand as can be seen in Table 8. The basecase scenario contains DLF and BACF as a pre-treatment for UF and is not tested during the research period. The goal of the experiments was to test the assumptions for the Flagship scenario and the worst case scenario, but also to see if the settings could be improved / enhanced.

Table 8: The different scenarios and the corresponding design.

	Unit	CW-pretreatment	No CW-pretreatment	DLF-BACF pretreatment
Flux	lmh	60	35	60
Filtrationtime	min	40	25	40
UF recovery	%	95%	85%	95%
CEB-chemicals		citric acid, NaOH, NaClO, HCl	similar	similar
Backwashing		Concentrate RO	Concentrate RO + UF permeate	concentrate 1st pass RO

Settings for a test with the UF would contain the following principles (in order to enhance the production):

- An increase in flux (increase the amount of water being pushed through the membrane).
- An increase in filtration time (and therefore decrease in BW-frequency).
- A decrease in CEB-frequency.

The latter should also result in a decrease in chemicals used (when the dosage is kept constant). An increase in flux or filtration time will result in a higher fouling rate of the membrane surface as more water is being pushed through the membrane. When a new flux or filtration time was tested, the process (permeability) was followed for an amount of time (preferred minimum 2 weeks) in order to decide whether the new setting resulted in a stable permeability.

In order to compare how the UF would perform with the constructed wetlands as a pre-treatment, the UF was operated with varying fluxes and filtration times on direct feed water sources without any form of pre-treatment (from May 2019):

- Direct Biox (t24 combined CEB, caustic > citric)
- Direct MBR (t24 combined CEB, caustic > citric)
- Direct Mix of MBR & Biox (t12 combined CEB, caustic > citric)

After the direct sources were tested on the UF, the constructed wetlands were connected so that the pre-treated water could be tested (start October 2020):

- Constructed wetlands > Biox (t24, t48 citric CEB; t72 caustic CEB)
- Constructed wetlands > MBR (t24, t48 citric CEB; t72 caustic CEB)
- Constructed wetlands > Mix (t24, t48 citric CEB; t72 caustic CEB)

Another interest of the research program was the use of RO brine as backwash water for the UF (start March 2021):

- Constructed wetlands Biox ;brine reuse (t24, t48 citric CEB; t72 caustic CEB)
- Constructed wetlands > MBR; brine reuse (t24, t48 citric CEB; t72 caustic CEB)
- Constructed wetlands > Mix; brine reuse (t24, t48 citric CEB; t72 caustic CEB)

During operation the UF was periodically cleaned with backwashes and CEB's according to the scheme in Table 9 . Chemicals during CEB's were dosed according to the following concentrations:

- Caustic CEB: NaOH 550ppm & NaOCl 245ppm.
- Citric CEB: $C_6H_8O_7$ 2000ppm.

During the tests with pre-treated water by the constructed wetlands, changes in the wetlands were linked to the performance of the UF as much as possible. A full overview of all the tests done with the UF can be seen in Attachment C.

Table 9: Backwash & CEB regime UF

Step (Backwash)	**Duration (sec)**	**Flux (l/h/m²)**
Air scour	30	
BW Bottom	30	120
BW Top	30	120
Forward Flush	30	40
Total duration	120	
Step (CEB)		
Air Scour	30	
Dosing 1	30	120
Dosing 2	30	120
Soak	900	
BW Bottom	60	120
BW Top	60	120
Forward Flush	60	40
Total duration	1170	

2.3.3 Ion-exchange (softener-scavenger)

2.3.3.1 Resins selection for experiments for softener and scavenger

As it has been mentioned already the IX treatment step in the full-scale design is expected to consist a softener and a scavenger IX columns in series. Research for the performance of IX treatment step was conducted as a part of the brackish water treatment line research from 2019 till 2021.

Initially, cation and anion resins to be research were selected. In case of cation resins, two major groups exist based on their functional group; the weak acid cation (WAC) and the strong acid cation (SAC) resins. Both are widely used for softening purposes. For a feed water with high salinity such as the mixed Biox and MBR effluent streams, a WAC resin would be the preferred option that can provide a constant product water quality and therefore operational stability. The WAC Amberlite HPR8300 H (HPR8300) resin was chosen to be used in the pilot research due to its TVC being greater than that of the MAC-3 that was initially chosen in the full-scale design. The WAC resins properties based on the product data sheet are available in Table 10.

Table 10: WAC Resin Properties

Resin Name	Amberlite HPR8300 H
Backbone	Acrylic
Matrix	Macroporous
Functional Group	Carboxylic Acid
TVC	4.70 eq/ L_R (H form)
Swelling (H → Na)	60%
Product Data Sheet	(1)

Evides Industriewater owns 4 (of which 3 operational) plants with a softener, being: DWP Maasvlakte, DWP Botlek, Mobile softener and BASF E-500 (under construction). However, all these softeners are using SAC resin. Design programmes like WAVE (Water Application Value Engine) can be used for the design of a WAC unit used as a softener. Thus, the main focus for the IX unit in the brackish water line research was towards the SBA resin's performance rather than the WAC resin's performance.

In case of the anion resin, two major groups exist based on their functional group; the weak base anion (WBA) and the strong base anion (SBA) resins. The WBA resins are active at a pH below 6. Since the mixed BIOX and MBR pilot feed has a pH of about 7.5 the use of a WBA resin has been excluded. Thus, SBA resins were considered for the pilot research. SBA resins can be either Type I with a functional group of benzyltrimethylammonium ($-CH_2-N(CH_3)^{3+}$) or Type II with a functional group of benzyldimethylethanolamine ($-CH_2-N(CH_3)_2(CH_2CH_2OH)^+$). They can have a styrene or an acrylic backbone and a gel or a microporous matrix.

The SBA resins of Table 11 were selected to be tested in the pilot research in order to find the optimal option for the full scale. Resins from most of the possible combinations of backbone, matrix and functional group of SBA resins were chosen.

Table 11: SBA Resin Properties

Resin Name	**Amberlite SCAV4 Cl**	**Amberlite IRA458 Cl**	**Amberlite HPR9100 Cl**	**Amberlite HPR9000 OH**
Backbone	Acrylic	Acrylic	Styrene	Styrene
Matrix	Macroporous	Gel	Macroporous	Macroporous
Functional Group	Type I	Type I	Type II	Type I
TVC	>≥ 0.80 eq/ L_R (Cl form)	≥ 1.25 eq/ L_R (Cl form)	≥ 1.1 eq/ L_R (Cl form)	≥ 0.8 eq/ L_R (OH form)
Product Data Sheet	(2)	(3)	(4)	(5)

Type II SBA resins with acrylic backbone were not tested because they do not exist. The upper limit for gel type resins with a styrene backbone is 1 g $KMnO_4$/ L_R/ batch (6). When calculating the organic loading on the resins, the result is 13.7 g $KMnO_4$/ L_R/ batch[8] for the mixed MBR and BIOX stream, respectively. Therefore, either Type I or Type II SBA resins with styrene backbone and gel matrix were not considered for the research.

2.3.3.2 Methodology followed in HPR8300 WAC resin, Amberlite SCAV4 Cl (SCAV4) and Amberlite IRA458 Cl (IRA458) SBA resins experiments with IX1 pilot (research 2020)

The SCAV4 and IRA458 resins were initially tested during a pilot study with IX1 pilot (Figure 6) that is located in the pilot hall of DeCO (Demineralisation and Cooling tower water) production plant at Hoek. The experiments performed have already been discussed in detail in the thesis report of Ioanna Gkoutzamani that can be found in TU Delft repository[9].

Figure 6: IX1 Pilot

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[8] For the calculation of this number the TOC of the mixed stream was 10.3 mg/L. The $KMnO_4$/TOC ratio used was 5.5 (11). The throughput per batch and the resin volume used based on the full scale design of sub-chapter 2.2.3 were 4000 m^3/batch and 16553 L_R, respectively.

[9] https://repository.tudelft.nl/islandora/object/uuid%3A88d753b7-bc82-4c3c-a7c7-ffc3e22d9201

The methodology followed for those experiments won't be repeated in this report, but only some important findings that were valuable for the continuation of the research will be mentioned in sub-chapter 3.3.1. It must be pointed out that the IX1 pilot feed water during the above-mentioned research was MBR effluent pre-treated with the only the UF pilot (no BIOX contribution and no constructed wetlands pre-treatment) (7).

2.3.3.3 Methodology followed in Amberlite HPR9100 Cl (HPR9100) and Amberlite HPR9000 OH (HPR9000) SBA resins experiments with IX1 pilot

A selectivity order experiment was performed with IX1 for the HPR9100 and HPR9000 SBA resins of Table 11. The HPR8300 WAC resin was placed in series prior to the SBA resins. The feed water of the pilot was a mixed MBR and BIOX effluent streams pre-treated with the constructed wetland and UF pilots. The main anion concentrations are available in Table 12. The production flow rate was 0.4 m^3/h per set of IX1 pilot. The production was monitored with an online NO_3^- analyzer, based on which the production was stopped and the resins were regenerated at a point that NO_3^- in product was approximately equal to NO_3^- in feed water. Moreover, product water samples were collected spread during production and were analyzed for HPO_4^{2-}-P and SO_4^- content.

Table 12: Feed Water quality during IX1 experiments with HPR9100 and HPR9000

Ions	Concentration (mg/L)	Concentration (meq/L)
NO_3^-	29	0.47
HPO_4^{2-}-P	0.7	0.04
SO_4^{2-}	95	1.98
Sum	-	2.49

The regeneration consisted of six up-flow steps and one down-flow step, seven steps in total. The first step was backwash of the WAC column. Then, a solution with 3.5% HCl was injected only to the WAC column in order to replace the removed ions with H^+ ions. The acid was displaced from WAC column with demineralized water. A second chemical solution containing 4% NaOH was injected into both the WAC and SBA columns in series. The purpose of this step was to replace H^+ ions of the WAC resin with Na^+ ions, but also the removed ions from SBA resins were partially replaced with OH^- ions. A third solution containing 8% NaCl was injected to both WAC and SBA columns in series. The purpose of this step was to replace the removed ions of SBA resin with Cl^- ions. Then, the excess chemicals from both columns were displaced with demineralized water. The final regeneration step prior to a following production was a down-flow prewash of both columns in series with demineralized water. Both the WAC and SBA resins beds were non-packed during regeneration. The regeneration setting for the WAC are available in Table 13 and for the two SBA resin in Table 14.

Table 13: WAC regeneration setting during IX1 experiments with HPR9100 and HPR9000

	HCl	NaOH
Regeneration Ratio (%)	105	105
Ch. Concentration (%)	3.5	4
Flow (BV/h)	10	7.7
Contact Time(min)	31	38.5

Table 14: SBA regeneration setting during IX1 experiments with HPR9100 and HPR9000

Resin	HPR9100	HPR9000
Resin Volume (L in Cl form)	19.5	19.5
Regeneration Level (g NaCl/ L_R)	80	80
Regeneration Ratio (%)	124	100
Ch. Concentration (%)	8	8
Flow (BV/h)	2.3	2.3
Contact Time (min)	26	26

2.3.3.4 Methodology followed in SBA-resin experiments with IX2 pilot

Based on the experiments performed with IX1 pilot unit it was decided that IRA458 was the most promising resin for the full-scale design based on the OC achieved and the product water quality. SCAV4 resin would be able to produce a similar product water quality but its OC was lower than IRA458. HPR9100 and HPR9000 resins were excluded from further research of their use in the full scale due to early HPO_4^{2-} breakthrough noted in product samples. All results that lead to the above conclusion are presented in sub-chapters 3.3.1 and 3.3.2.

The continuation of the IX research was performed with a newly constructed in 2020 pilot named IX2 pilot. As mentioned above the research should have been continued with HPR8300 as the WAC resin and IRA458 as the SBA resin. However, by the time the IX-2 pilot was constructed and delivered (2019) the research with IX1 pilot was not finished due to technical delays. In 2019 SCAV4 was chosen to be used in IX2 pilot. Therefore, it was decided to start the research on IX2 with SCAV4, since still a lot of knowledge could be obtained for the full-scale design. Thus, IX2 pilot was operated with SCAV4 as the SBA resin from late December 2020 till mid-May 2021. Then, the SBA resin column of IX2 pilot were changed to IRA458 and the experiments presented in this report took place from end May 2021 till beginning of August 2021.

Pilot description and monitoring

The IX2 pilot consists of three identical sets (Figure 7). Each set consists of two columns. The first column for all three sets was filled with the HPR8300 WAC resin. The second column was filled initially with SCAV4 SBA resin and later own with IRA458 SBA resin.

Three chemical tanks (HCl, NaOH and NaCl) are located on the pilot's skid. One production pump is assigned per set (three in total). Two service water pumps are used for the regeneration and three pumps from the different regeneration chemicals are also located on the pilot.

Online automatic measuring devices of flow, EC, pressure and temperature are placed in the influent stream. Also, online automatic measuring devices of pressure, EC, and pH exist in the streams between the WAC and the SBA columns and in the product stream (after SBA). Automatic and non-automatic sampling points can be found in the influent, the stream between the WAC and SBA columns and the product streams.

The mixed product stream from the two or occasionally three sets in production was sent to an online NO_3^- analyzer (UV400, Tethys) and an online HPO_4-P analyzer (AMI Phosphate-II, Swan). For a short period of time during the research a second online HPO_4-P analyzer (AMI Phosphate-II, Swan) was accepting the feed water of the pilot. Also, the NO_3^- concentration in the product of the constructed wetlands, which was basically the same in IX2 feed (since UF does not remove NO_3^- ions), was measured with an online analyzer (NX7500, Hach).

Figure 7: IX2 Pilot

IX2 feed samples were collected in a weekly basis and were analyzed for a series of water quality parameters (e.g EC, pH, TOC, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, NO_3^-, HPO_4^{2-}-P and more) by Aqualab Zuid. Moreover, two times per week extra IX2 feed samples were collected and the content of NO_3^- and HPO_4^{2-}-P was measured with Hach test kits. Finally, the SO_4^{2-} concentration of the IX2 feed water was measure with Hach test kits at least 4 times per week.

WAC- and SBA-resin volumes used in IX2 pilot

In Table 15, Table 16 and

Table 17 the resins volumes used in the three sets of IX2 pilot are given for HPR8300, SCAV4 and IRA458, respectively.

Table 15: HPR8300 WAC resin volumes used in IX2

	Set 1	Set 2	Set 3
Bed Depth in H^+ form (L)	147	148	148
Bed Depth in Na^+ form (L)	235	235	235
Total Load (Eq)	691.1	697.5	697.5
WAC Bed Depth in H^+ form (m)	1.08	1.09	1.09
Inert Volume (L)	54	54	54
Inert Bed Depth (m)	0.4	0.4	0.4

Table 16: SCAV4 SBA resin volumes used in IX2

	Set 1	Set 2	Set 3
Bed Depth in Cl^- form (L)	380	384	381
Total Load (Eq)	303.8	306.9	304.6
SBA Bed Depth (m)	1.56	1.58	1.57
Inert Volume (L)	73	73	73
Inert Bed Depth (m)	0.3	0.3	0.3

Table 17: IRA458 SBA resin volumes used in IX2

	Set 1	Set 2	Set 3
Bed Depth in Cl^- form (L)	375	375	375
Total Load (Eq)	468.8	468.8	468.8
SBA Bed Depth (m)	1.54	1.54	1.54
Inert Volume (L)	73	73	73
Inert Bed Depth (m)	0.3	0.3	0.3

Feedwater of IX2 pilot

The goal feed water for the brackish water line (CW à UF à IX2 à RO) was a mixed stream of 50/50 MBR and Biox effluent. However, there were periods of time that the one or the other source was not available. These periods will be pointed out during the results section. Also, there were some runs that only MBR or Biox was used as feed on purpose in order to investigate differences on pilot operation for the two feed streams.

The concentration for the most interesting parameters for the IX operation in case of mixed 50/50, MBR and Biox are given in Table 18. These values are the averages based on the water quality analyses of MBR and Biox from January till July 2021. It must be noted that these values are the MBR, Biox and mixed water qualities without pre-treatment with CW and UF. However, after pre-treatment with CW and UF none of the below mentioned components changes significantly, expect of SO_4^{2-} that after the CW can be higher by 20% in the start of the operational time (first two years based on pilot experiments). This leaching effect is expected to become less over time. But this effect is valid for all three streams, after treatment with the CW.

Table 18: IX2 feed water quality

Feed source	**Mixed**		**MBR**		**Biox**	
pH	**7.5**		**7.5**		**7.5**	
EC (µS/cm)	**1175**		**1450**		**900**	
TOC (mg/L)	**10.3**		**10.1**		**10.5**	
Unit	**mg/L**	**meq/L**	**mg/L**	**meq/L**	**mg/L**	**meq/L**
Cl^-	197	5.57	292	8.25	102	2.88
HCO_3^-	212	3.43	250	4.00	174	2.86
NO_3^-	23.5	0.38	40.5	0.65	6.5	0.1
HPO_4^{2-}-P	0.95	0.06	1.5	0.1	0.4	0.02
SO_4^{2-}	99.5	2.00	83	1.75	116	2.4
Ca^{2+}	65	3.24	70	3.47	60	3
Mg^{2+}	15.5	1.25	21	1.73	10	0.8

An important difference between the MBR and BIOX that can have an effect on SBA resins performance, is the high content of Cl^-, HCO_3^-, NO_3^- and HPO_4^{2-}-P in the MBR (3, 1.2, 6.5 and 5 times higher than Biox). Simultaneously the content of SO_4^{2-} in MBR is 30% lower than in Biox.

Production and regeneration settings

The production flow rate in all experiments was at 2,670 L/h per set. The goal was to always have at least two sets in parallel production and the third set to be in the meantime regenerated and be kept in standby. When one of the two sets was exhausted then the standby set should start its production and the exhausted set should be sent for regeneration. In this way, enough product water would always be available for the operation of the RO pilot units.

The determination of the exhaustion point of each set was based on the HPO_4^{2-}-P concentration in the mixed product water of the producing sets. The rule was the following:

"If the HPO_4^{2-}-P concentration in the mixed product stream was above a given set point (usually half the feed HPO_4^{2-}-P concentration – 0.3 mg P/L), the longest running set was considered exhausted and it was sent for regeneration".

However, the software required for this control system was not available from the start of the experimental period and it was built after the first month of operation. Thus, during the first month of operation the productions of the sets were control and stopped based on their production time.

The regeneration steps for both the WAC and the SBA columns during the pilots experiments were are presented in Table 19. In Table 20 the target stoichiometry and the chemicals content for the WAC resin regeneration is given. It must be noted that after a certain point in the research (it will be noted in the results chapter) the equivalents of Na^+ dosing (NaOH) was half of the H^+ dosed (HCl) from which point also the flowrate of this step had to be reduced to 1,400 L/h and the NaOH content had to be reduced to 2.5 % in order to increase the contact time to 14 min. Moreover, it should be pointed out that the HCl and NaOH dosing was set in the software in grams of chemicals calculated based on the target stoichiometry over the expected passed equivalents. However, the passed equivalents were different in different runs depending the operation of the SBA columns and thus the final achieved stoichiometries differ over different runs. Specific values will be presented in the result chapter. For the regeneration of SBA resin, two chemical dosing were tested. These were 60 and 80 g NaCl/L_R. The chemical content for the SBA regeneration was kept stably at all experiments at 5% NaCl (Table 21). In one run the option to dose simultaneously the NaOH and NaCl through both WAC and SBA columns in series (first through WAC) based on the full-scale design was tested. Thus, at that run steps 4 and 5 were combined with a flow of 1,400 L/h.

Table 19: Regeneration steps in IX2 pilot

		Column(s)	**Direction**	**Flow rate (L/h)**	**≈Duration (h)**
1	Backwash	WAC and SBA	Upward	1,357	0.5
2	HCl dosing	WAC	Downward	1,085	0.5
3	Displacement	WAC	Downward	1,085	0.3
4	NaOH dosing	WAC	Upward	1,700[10]	0.5
5	NaCl dosing	SBA	Upward	1,400	0.3
6	Displacement	WAC and SBA	Upward	1,700	1
7	Settling/bed rest	-	-	-	0.17
8	Prewash	WAC and SBA	Downward	1,700	0.5
	Total	-	-	-	3.77

Table 20: Chemical dosings – WAC regeneration in IX2 pilot

Chemical	**HCl**	**NaOH**
Stoichiometry (%)	105	105
Chemical content (%)	4	3[11]

Table 21: Chemical dosings – SBA regeneration in IX2 pilot

Chemical	**NaCl**	
Option	**Min**	**Max**
Chemical dosage (g NaCl/ L_R)	60	80
Chemical content (%)	5	5

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[10] In Run 3 and Run 7 of SCAV4 performed the flowrate had to be reduced to 1400 L/h to increase contact time and kept at this level for all research with IRA458.

[11] It was reduced to 2.5% half way Run 7 of SCAV4 and kept at this level for all research with IRA458 to increase contact time at 14 min despite the lower dosing.

2.3.3.5 Methodology followed in SCAV4 and IRA458 SBA resins experiments with IX1 pilot (research 2021)

Experiment at different regeneration levels for SCAV4 and IRA458were performed with IXI. The feed water of the pilot was a mixed MBR and BIOX effluent streams pre-treated with the constructed wetland and UF pilots. An important difference with other experiments with the either one of the IX pilots was that WAC columns were not used and the water was directly treated by the SBA resins without initial softening. The production flow rate was 0.4 m^3/h per set of IX1 pilot. The production was monitored with an online HPO_4^{2-}-P analyzer, based on which the production was stopped and the resins were regenerated at a point that HPO_4^{2-}-P in product was equal to 0.3 mg P/L (about half the HPO_4^{2-}-P concentration in feed water).

The first regeneration step was the dosing of 5% NaCl to the SBA resin in an up-flow direction. Two regeneration levels were tested; (i) 80 gr NaCl/L_R and (ii) 60 gr NaCl/L_R[12]. The excess chemical was displaced with demineralized water (up-flow). The final regeneration step prior to a following production was a down-flow prewash with demineralized water. Inert was added to the SBA resins columns so as to keep the resin beds packed during regeneration. The regeneration setting for the two SBA resins are given in Table 22.

Table 22: SBA regeneration setting during IX1 experiments with SCAV4 and IRA458

Resin	**SCAV4**		**IRA458**	
Resin Volume (L in Cl form)	25		25	
Regeneration Level (g NaCl/L_R)	80 (in reality 90)	60 (in reality 70)	80	60
Regeneration Ratio over TVC (%)	170	128	110	82
Ch. Concentration (%)	5		5	
Flow (BV/h)	3.7		3.7	
Contact Time(min)	26	19	26	19

2.3.4 Reverse-osmosis

The RO pilot consists of 3 RO sub-pilots that can be CIP'ed with an automatic CIP unit:

- One single membrane module that is used as a **biofouling guard**. It receives the IX2 product as feedwater and represents the first membrane. Effects of particulate matter, organic fouling (deposition of biopolymers on the membrane surface) and biofouling (bio growth in the feed spacer) are monitored. A cartridge filter (10µm) is placed before the membrane;
- One bigger RO module with 2 arrays (**RO-Groot**). The first array has two times 5 membranes in series and a second array with 5 membranes. The pilot also receives the IX2 product as feedwater and is used to produce enough water for the last module. A cartridge filter (10µm) is placed before the membrane;
- One single membrane pilot that is used as a **scale guard**. It receives the concentrate of RO-Groot as feedwater and represents the last membrane. Effects of scaling (precipitation in the feed spacer and on the membrane surface of components that exceed their solubility limit) because of increased salinity are monitored. A part of the concentrate is being recycled to the feed to obtain the high salinity of the last membrane;
- The **CIP-uni**t is used to perform a base or acid cleaning of the membranes. The efficiency of the cleaning is a function of the conditions (concentration, pH, temperature), the exposure time and the turbulence in the feed spacer. The CIP is regulated based on chemistry (pH) and time.

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[12] Later on it was found that issues with the NaCl dosing pump resulted in higher dosing only toward SCAV4. Specifically, on average 90 and 70 gr NaCl/Lr were dosed instead of 80 and 60 gr NaCl/Lr.

The main issues that occur in reverse osmosis are fouling and scaling. To be able to predict operational issues and reduce costs in the full-scale operation, these effects are monitored. The focus of the RO pilot is to determine if the RO can be operated with the suggested settings without permanent fouling and is able to meet the required product quality. In addition to the operational settings and water quality, energy and chemical consumption is calculated and the salt passage is being monitored to indicate lifetime of the membranes. The energy consumption of the RO units is mainly in the high-pressure pump. The chemistry consumption will consist of the chemistry required for the RO CIP.

Monitored KPI's and quality parameters:

- Normalized pressure difference (NPD, continuous): Indicator for the fouling of the feed spacer
- Mass transfer coefficient (MTC, continuous): Indicator for the fouling of the membrane
- Normalized salt passage (NSP, continuous): Indicator for the rejection of the membrane
- Energy consumption (kWh/year, continuous)
- Chemical use (kg/year): based on CIP frequency
- Retention TOC (DOC, biopolymers (BPC-14), humic substances, building blocks, LMW neutrals, via sampling)
- Product quality: via sampling and continuous conductivity measurement

2.3.4.1 Selection of pilot settings

The best pilot design was selected based on 4 different factors: Product quality, representation of the full-scale (flux, recovery, cross-flow), influence of recycle and possibility for the observation of scaling potential and biofouling potential.

In order to operate the pilot installation with an identical recovery, flux and minimal crossflow to the full-scale design, recycle of a part of the condensate stream is necessary. This has an impact on the nutrients and salts that are being send to the first membranes of the pilot. Therefore, it was decided to operate RO Groot without recycle and simulate a recovery of 85% on the last membrane with applying recycle. The minimal cross-flow of the full-scale design was translated to the 4-inch pilot configuration and was set on 1.14m³/h. The set-up of the pilot configuration is shown in Figure 8.

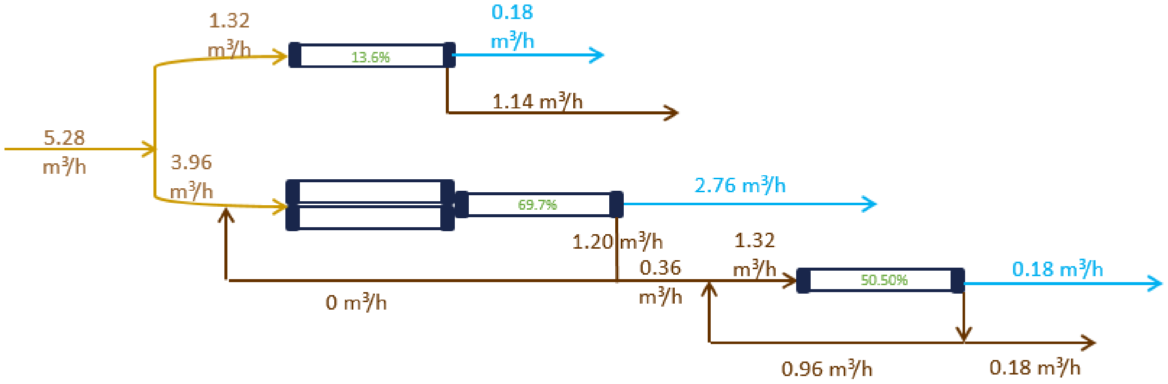


Figure 8: Selected pilot set-up (yellow = feedwater, blue = permeate, brown = concentrate).

2.3.4.2 Consideration and choice of membrane type

In Table 23 the properties of the full-scale membranes are compared to the available 4-inch membranes for the pilot installation with comparable characteristics.

Table 23: Different membrane types and characteristics. [1] Permeate flow and salt rejection based on the following test conditions: 2,000 ppm NaCl, pressure specified above, 77°F (25°C) and 15% recovery. [2] Elements must be conditioned prior to start-up. A one-time flux loss will occur during stabilization. Listed values apply after performance stabilization. [3] Permeate flows for individual elements may vary +/-20%.

	Element	Active area (m^2)	Pressure (bar)	Flow[1] (m^3/d)	Rejection (%)	Feed spacer (mil)	Diameter (inch)	Permeability
Full-scale design	ECO PRO 400i	37.2	10.3	43.5	99.7	34	8	0.0047304
Pilot Alternative 1	LC LE-4040	8.73	8.6	9.5	99.2	28	4	0.005272295
Pilot Alternative 2	LC HR-4040	8.7	15.5	11	99.7	28	4	0.003398838
Pilot Alternative 3	BW30-4040	7.2	15.5	9.1	99.5	34	4	0.003397551
Pilot Alternative 4	HSRO-4040-FF	8.4	10.3	7.2	99.5	34	4	0.003467406

Based on the above characteristics and availability the LC LE-4040 was selected as best alternative to use in the pilot. This membrane however has a smaller feed spacer (28mil) compared to the full-scale membrane that has a 34mil feed spacer. Due to the smaller size, biofouling is more likely to occur than with a 34mil feed spacer. The effect of this on the research is strongly related to the amount of biofouling that will occur during the research. If little biofouling occurs, it can be concluded that the feedwater will also cause minimal biofouling on the 34 mil feed spacer. If strong biofouling does occur, it can be considered to also test the BW30-4040 membrane with equal feed spacer size (keeping in mind same quality of the feed water plus other indicators such as temperature while testing).

2.3.4.3 Differences and limitations in the pilot set-up

To understand the results obtained with the pilot installation and to predict the outcome in the full-scale, it is important to know the differences between both installations and understand the impact of these differences. An overview of the parameters of full-scale and pilot-scale are shown in Table 24.

Table 24: Comparison between pilot-scale and full-scale design

Parameter	Full-scale DeCo 2.0	Pilot BWL	Factor
Membranes	ECO PRO 400i (8'')	LC LE-4040 (4'')	0.5
Porosity	0.00473	0.00527	1.11
Feed spacer	34mil	28mil	0.82
Salt passage	99.7	99.2	0.99
Total active surface area	11,593.92m^2	139.72m^2	0.012
Flux	21LMH	21LMH	1
Recovery	85 %	85 %	1
Cartridge filter	None	10µm	/
Dosing	None	None	/

RO-Groot further has a limited number of sensors. Therefore, it is not possible to measure the flux of array 1 and array 2 separately. The flux over the whole pilot has to be looked at. Also NSP cannot be measured accurately for each array. Next to that, the real recovery of the pilot is not 85%, but lower. Therefore also the total concentrate and permeate produced in the pilot have a somewhat different quality than in the situation of 85% recovery.

2.3.4.4 Normalization and reference values for operation – WAVE

Because of influence of temperature and fouling of the membranes, the necessary feed pressure will differ to keep the flux a constant. To obtain insight in the influence of fouling and be able to compare the results, the data must be normalized to a standard temperature. To determine the normalization factors for each pilot, the modelling program WAVE was used. In Table 25 the normalization factors for each pilot are given. For this research, a reference temperature of 25°C has been chosen, because this is commonly used in a full-scale installation. An overview of the selected correction factors is given in Table 25:

Table 25: Selected normalization factors

Correction factor	Full-scale	Method	Biofouling guard	RO-groot	scaleguard
m	1.6 (commonly used)	ROSA	1.27	1.27	1.27
n	0.4 (commonly used)	ROSA	0.56	0.56	0.56
$Q_{vc,ref}$ (m^3/u)		Installation	1.23	2.58	1.23
U	3728	ROSA	3742	3634	3765
$Q_{p,ref}$ (m^3/u)		Installation	0.18	2.76	0.18
Osm feed		Feedwater	0.0328	0.0328	0.0328
Osm perm		Feedwater	0.0157	0.0157	0.0157
Osm conc		Feedwater	0.0394	0.0394	0.0394
T_{ref} (°C)	25	10 or 25	25	25	25

WAVE can also be used to simulate expected performance of the pilots. Several runs for different fouling factors were performed with the selected settings to see the expected values of important KPI's and the operation of the pilots. The results of the different KPI's are shown in Table 26. A feedwater temperature of 19.1°C, which is assumed to be the average yearly temperature, was used and it is assumed that the permeate flows away free to the atmosphere.

Table 26: Simulation of different KPI's for FF 1 (=new membrane), 0.8 (wanted yearly average) and 0.69

	Selected flow factor	NPD	MTC	NSP	P_{feed}	EGV permeate	specific energy
	%	bar	m/s.Pa	(-)	bar	µS/cm	kWh/m^3
Biofouling guard (recovery = 13.6%)	FF 1	0.15	2.09	1.67%	4.3	23.00	1.17
	FF 0.8	0.15	1.66	1.58%	5.2	22.76	1.39
	FF 0.69	~~0.08~~	1.41	1.68%	5.9	23.08	1.61
RO Groot (recovery = 69.7%)	FF 1	1.53	2.04	2.03%	5.7	43.30	0.30
	FF 0.8	1.53	1.64	1.99%	6.6	42.44	0.34
	FF 0.69	1.53	1.40	1.97%	7.3	41.96	0.38
Scaleguard (recovery = 50.50%)	FF 1	0.18	1.80	3.21%	7.7	184.24	2.06
	FF 0.8	0.18	1.46	3.21%	8.9	184.24	2.28
	FF 0.69	~~0.09~~	1.30	3.21%	9.6	184.24	2.44

When the flow factor is decreasing this means that part of the pores is being fouled and thereby blocked, causing the MTC to drop and the feed pressure and specific energy to rise. A fouling factor of 0.8 will result in a 20% decrease in MTC, while a fouling factor of 0.69 will result in a 30% decrease of MTC. Further, no scaling issues are predicted by the program. NPD is normally not affected by changing the fouling factor, but simulation for a single membrane module gives an off-set. It can be assumed that NPD for the biofouling guard is 0.15 bar and NPD for the scaleguard is 0.18 bar.

3. RESULTS & DISCUSSION

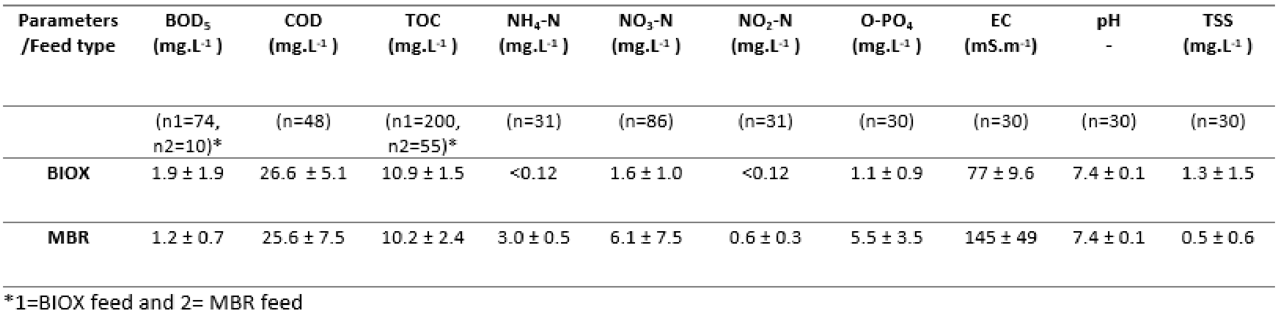
3.1 Wetlands

Three summary reports have been issued by Ghent University (Hafiz Khan, Diederik Rousseau) describing findings and conclusions on the different modes of operation. These reports are used for this conclusive summary.

- DOW/EVIDES PILOT WETLANDS REPORT 1 (07/2019-01/2020)
- DOW/EVIDES PILOT WETLANDS REPORT 2 (01/2020-09/2020)
- DOW/EVIDES PILOT WETLANDS REPORT 3 (Final) (09/2020-07/2021)

Also, a parameter scan was made to address the effect of the wetlands on all measured parameters. Some additional results of experiments or general observations are summarized in reports from the HZ-University (Mireille Martens, Lies Hamelink) or quarterly reports/presentations. Results of the micropollutant sampling and the biofouling potential analyses have been received from the contract labs and summarized in presentations.

Table 27: Wastewater characteristics (average ± SD) of some important parameters for both feeds (BIOX and MBR)



Parameters /Feed type	BOD_5 ($mg.L^{-1}$)	COD ($mg.L^{-1}$)	TOC ($mg.L^{-1}$)	NH_4-N ($mg.L^{-1}$)	NO_3-N ($mg.L^{-1}$)	NO_2-N ($mg.L^{-1}$)	O-PO_4 ($mg.L^{-1}$)	EC ($mS.m^{-1}$)	pH -	TSS ($mg.L^{-1}$)
	(n1=74, n2=10)*	(n=48)	(n1=200, n2=55)*	(n=31)	(n=86)	(n=31)	(n=30)	(n=30)	(n=30)	(n=30)
BIOX	1.9 ± 1.9	26.6 ± 5.1	10.9 ± 1.5	<0.12	1.6 ± 1.0	<0.12	1.1 ± 0.9	77 ± 9.6	7.4 ± 0.1	1.3 ± 1.5
MBR	1.2 ± 0.7	25.6 ± 7.5	10.2 ± 2.4	3.0 ± 0.5	6.1 ± 7.5	0.6 ± 0.3	5.5 ± 3.5	145 ± 49	7.4 ± 0.1	0.5 ± 0.6

*1=BIOX feed and 2= MBR feed

3.1.1 Aeration strategy

During the first year of the pilot, the focus was on finding the optimal aeration strategy for COD and Nitrogen removal. Normally, COD removal will increase with abundant oxygen present. Also, for the nitrification process, where ammonium (NH_4^+) is oxidized to Nitrate (NO_3^-) there should be a certain level of oxygen present. For denitrification, where Nitrate (NO_3^-) is converted to N_2, anoxic conditions and sufficient degradable carbon are needed. From July 2019 till July 2021 different aeration strategies are tested and summarized in the reports of Hafiz Khan and Diederik Rousseau (Table 28).

Table 28: Different phases of aeration strategies along with feed type in wetland North and South.

	Number of days per phase	Aeration/DO Strategies	North Feed	South Feed	Biochar zone status
Phase 1	14	Continuous aeration (100%)	± 50/50% Mixed	± 50/50% Mixed	Active
Phase 2	23	50%-time (30 minutes) ON/OFF	± 50/50% Mixed	± 50/50% Mixed	Active
Phase 3	07	DO level setting at 3-4mgO$_2$.L^{-1}	BIOX	MBR	Bypassed
Phase 4	85	DO level setting at 2-3mgO$_2$.L^{-1}	BIOX	MBR	Bypassed
Phase 5	09	DO level setting at 1-2mgO$_2$.L^{-1}	BIOX	MBR	Bypassed
Phase 6	57	DO level 2-3 in zone 1 and 0 mgO$_2$.L^{-1} in zone 2&3	BIOX	MBR	Bypassed

The different aeration strategies impact the energy consumption needed for blower operations as shown in the graph below. Continuous aeration or a 50%on-50%off aeration does not seem to have a major influence on oxygen concentrations. Continuous aeration is wasting energy, set-point aeration works well. Based on the COD and nutrient removal efficiencies, it was concluded that setpoint aeration (2-3 mg/L) in the first zone provided sufficient oxygen with most efficient use of energy.

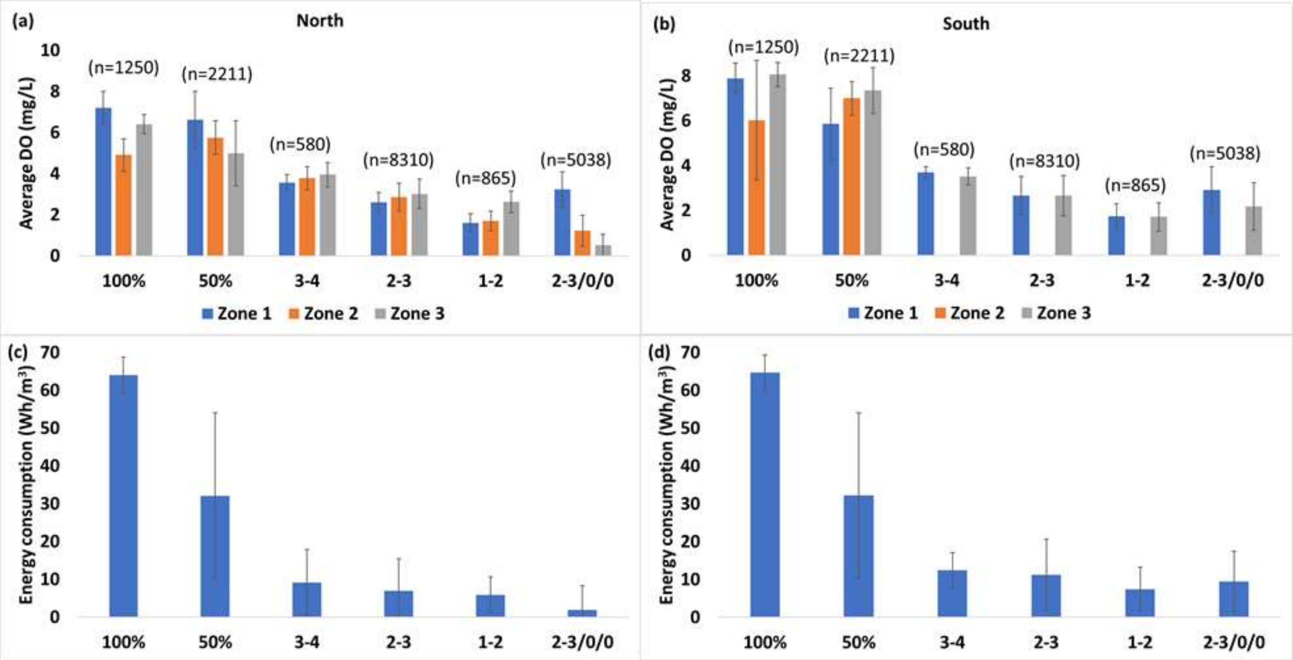


Figure 9: Average DO concentration and energy consumption per aeration setting for both wetlands (note: there are no data for zone 2 of wetland South during phases 3-6 as the biochar zone was bypassed)

Continuous aeration or a 50%on-50%off aeration does not seem to have a major influence on oxygen concentrations. Continuous aeration is wasting energy. Set-point aeration works well.

COD removal

In the table below the COD removal efficiencies are given for the different phases. For the first two phases, the COD in the effluent was lower than the detection limit of the COD-method used (LOD: 20 mg/L) and results were arbitrary set at 10 mg/L. For south phase 1, the removal efficiency is also questionable. Variations in temperature, seasons and vegetation during the various phases are mentioned as possible contributing causes for variations between north/south and the different feedstreams.

Table 29: COD removal efficiencies (%) in different phases of aeration along with feed type in wetland North and South

	North	**South**
	(%)	**(%)**
Phase 1 (100%)	> 61.3 (Mixed)	> 60.3 (Mixed)
Phase 2 (50%)	> 61.3 (Mixed)	> 60.3 (Mixed)
Phase 3 (3-4/0/0)	30 (BIOX)	18.8 (MBR)
Phase 4 (2-3/0/0)	33.2 (BIOX)	18.2 (MBR)
Phase 5 (1-2/0/0)	10.6 (BIOX)	1 (MBR)
Phase 6 (2-3/0/0)	14.9 (BIOX)	12.5 (MBR)

During 2020/2021, various aeration settings have been tested where 1st and 3rd zone were aerated. Differences in feed type, flow, temperatures, seasons will influence the results but on average COD removal% of 20-30% can be achieved with aeration 2-3 mg/L in the first zone and 1-2 mg/L in the third zone. Results can be retrieved in the presentations from Khan/Rousseau during the monthly R&D meetings.

NH4/NO3-removal

In the graphs below Nitrate/Nitrite/Ammonium concentrations are given for the different phases. In general, it can be concluded that all aeration settings result in complete to almost complete nitrification of the ammonium. During some upsets at the MBR, high concentrations of ammonium were received. In that case, NH_4 was detected in the effluent. Denitrification will be promoted at lower oxygen concentrations.

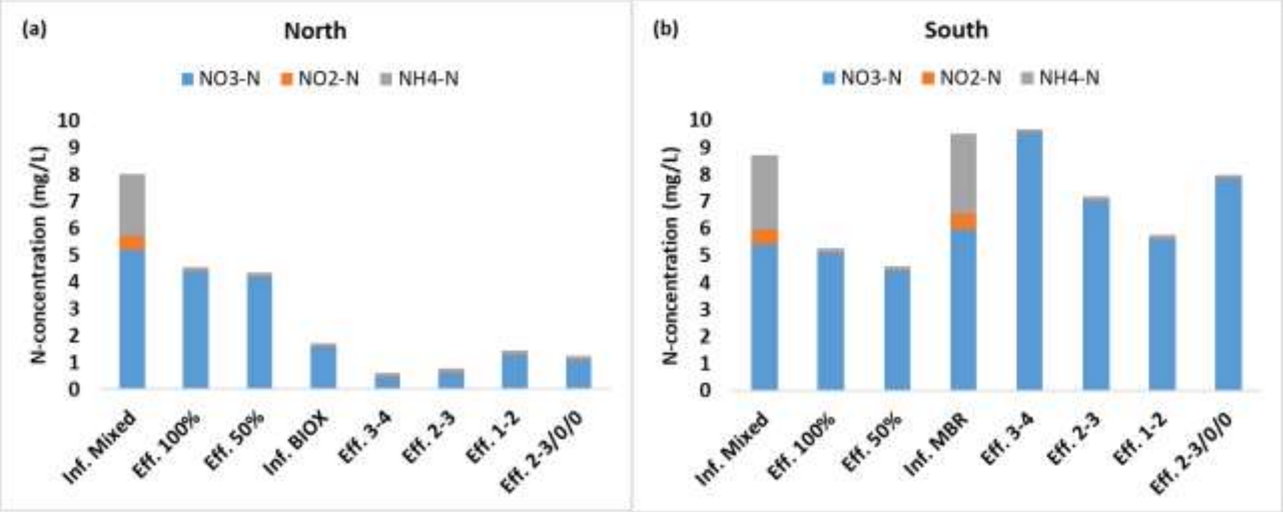


Figure 10: TN as a sum of NO_3-N, NO_2-N, and NH_4-N against each phase in both wetlands.

Various oxygen settings have been tested during the 2 years of operation. In report 3 of Khan and Rousseau concluded:

- Nitrification of ammonia happens at most oxygen settings, most of the ammonia is converted in zone 1.
- Denitrification is limited with MIX feed or MBR feed, even with blowers off in zone 2 and 3.
- Biox feed only showed more denitrification, but overall levels are lower which makes it difficult to decide on optimal aeration settings.

3.1.2 Carbon dosing

One of the main functions of a constructed wetland is the (partial) removal of nutrients. Experiments showed a near to complete nitrification of ammonia and based on the aeration settings a partial removal of nitrate (denitrification). Experiments were performed to determine the use of a carbon source to enhance nitrate, and thus total nitrogen, removal in the wetlands. The results and experiments are fully explained in the paper written by Hafiz Khan[13]. To summarize the results, with increasing COD/N-ratio comes increasing nitrate removal, resulting in a lower N-total in the effluent.

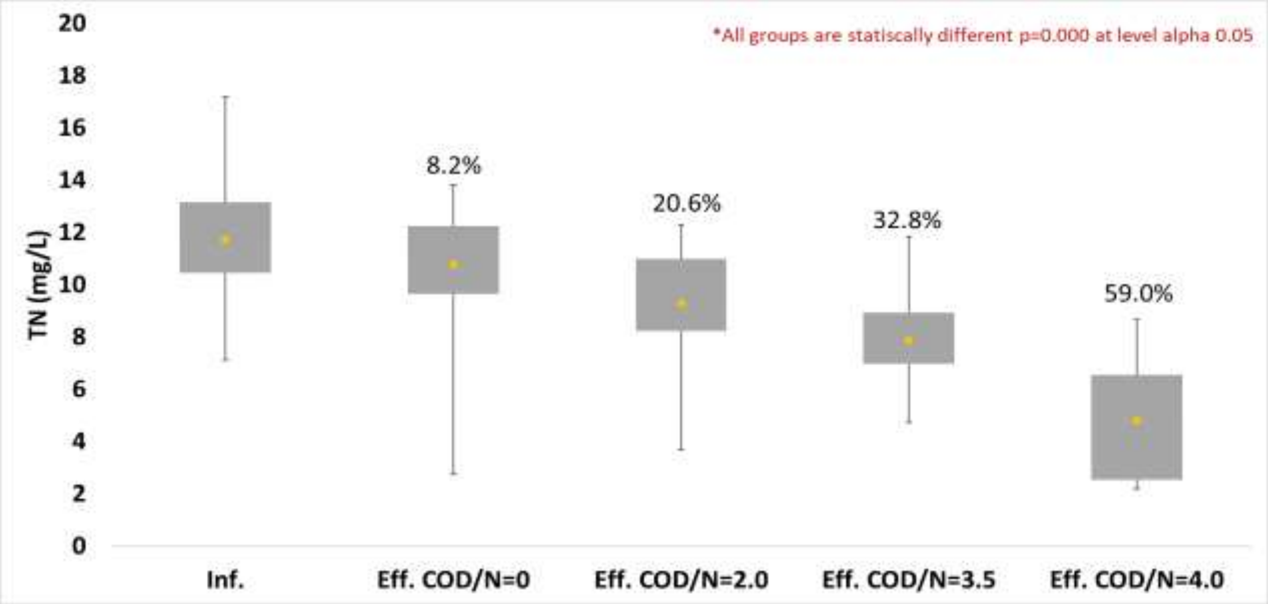


Figure 11: Effect of additional carbon dosing on wetland performance.

During the experiments, many practical issues were faced. The original C-source (Brenntaplus VP-1) had to be diluted to make it pumpable. In the original set-up the mix of C-source and influent was sprayed over the middle section of wetland North resulting in possible exposure of the surrounding area and operators, especially in windy conditions. With higher C/N ratios, more C-source is dosed which lead to local overdose and subsequent excessive biomass formation. This blocked part of the wetland and caused local flooding. After stopping the C-dose experiments, the effect of the excessive dosing could be observed for many weeks in elevated COD and less overall hydraulic conductivity.

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[13] Effect of carbon dosing on denitrification in an aerated horizontal subsurface flow constructed wetland receiving high hydraulic load, Khan et al. 2021

12 Effect of controlled aeration on COD and nitrogen removal in aerated horizontal subsurface flow constructed wetlands used for effluent polishing, Khan et al. 2021

A study was performed to determine the economic feasibility of removing nitrate in the wetlands, as opposed to nitrate removal via the scavenger resin (CITE). Evaluation showed that nitrate removal via ion-exchange was more effective. Not only would it be a better option economically, also the practical issues related to dosing carbon (clogging, excessive biomass growth, extra COD in product water) seem in favor of nitrate removal via IX.

3.1.3 Biochar

Biochar is a charcoal produced by pyrolysis of biomass/biomass waste under oxygen limited conditions. By applying certain activation processes, specific adsorption behavior can be introduced. In wetland south a 4.5m wide zone was created where 15% biochar (Verora GmbH, Edlibach, Switzerland, 80-90% C-content) was mixed with the Leca aggregates. More information on the type of biochar is given in the paper of Khan et all.[12] The zone could be bypassed. Based on various experiments and data evaluations, Khan summarized the role of the biochar zone in Report-3 for Dow/Evides. "The biochar zone showed disappointing results in terms of removal of COD, TOC, P and also other micropollutants, which is in stark contrast to the many positive results mentioned in literature." The fact that biochar is a very variable material, where properties depend on used feedstock and activation procedures and the use of this material in a less controlled environment with respect to mixing, temperature, are possible reasons for the lack of positive results. Specific activation procedures to improve performance in a full-scale wetland are not recommended because of complexity and the large amounts needed resulting in significant additional costs.

3.1.4 Micropollutant removal

In the course of the pilot, 4 studies have been conducted on identification and removal of micropollutants in the wetlands. An extended summary for all four studies has been prepared.

Round 1: May/June 2019, Aqualab Zuid report: ORG_2019_LC-QTOF_004.

Grab samples from both influents and both effluents have been taken over the course of three weeks (12 samples in total). Both wetlands were fed with Biox effluent. Following analyses have been conducted.

a. Suspect screening on a defined set organic micropollutants (drugs and pesticides)
b. Library screening on 2000 components in the library
c. Screening on unknown micropollutants

With the suspect screening, only metformine has been detected in all samples. The fact that none of the other 'suspects' , either drugs or pesticide related micropollutants, were detected in the influent and effluents can be explained by the feed flow. The 'suspects' are normally found in the effluent of municipal wastewater treatment plants and not in the effluent of industrial wastewater treatment plants. Presence of metformine (estimated concentrations 0.3-3 µg/L) in the industrial effluent is not very likely, there may be other similar organics with same gross formula present in the industrial effluent. There is also a possibility that small amounts of the suspected components are introduced via the industry water used at Dow which is surface water.

With the library screening, 2000 components can be identified. Small amounts of various drug/pesticide micropollutants were detected. Except for 4 and 5-Methyl-1H-benzotriazole, all estimated concentrations were <10 ug/L (concentrations relative to the internal standard with known concentration). By using calibration standards of 4 and 5-Methyl-1H-benzotriazole, the actual concentrations were determined ~5 to 50 ug/L. For the 4 and 5-Methyl-1H-benzotriazoles, removal efficiencies varied between ~90% and ~80%. One reason could be that adsorption capacity has been reduced in the course of the three weeks. Grab samples from the influent and effluent are taken at the same time, not taking into account the residence time of the water in the wetland. Variation in the influent concentrations therefore can lead to difficult to interpret removal efficiencies

The LC-MS screening showed a variety of other peaks that were not in the MS-library. Influent and effluent samples were compared and for component peaks that show a reduction over the wetland, the gross formula is reported. Exact identification would need more investigation and was not requested.

Round 2: October 2019, Aqualab Zuid report: ORG_2019_LC-QTOF_010.

Grab samples from both influents and both effluents have been taken over the course of three weeks (12 samples in total). Wetland North was fed with Biox effluent, Wetland South was fed with MBR effluent. A library screening on 2000 components has been conducted where concentrations are estimated based on relative responses towards an internal standard.

For wetland North (fed with Biox), the 1-H-benzotriazole and the 4 and 5-1H-Benzotriazoles were present at detectable concentrations (>0.1 ug/L relative to an internal standard). As mentioned in the June 2000 report, real concentrations may differ because sensitivity of the internal standard will differ from the components of interest. However, it is possible to calculate removal factors for these components. For the most abundant component (4 and 5-1H-MBTZ), there is a decrease in concentrations for two of the three series and an increase for one series. This could be caused by a saturation of the wetland for these components, an equilibrium exists between adsorption/desorption. Other possibility is a variation in influent concentrations combined with the sampling protocol where influent and effluent are sampled at the same time.

As expected, many more compounds were found in significant relative concentrations (0.1-1 ug/L). These are mainly (metabolized) drugs, as well as a pesticides. Removal efficiencies vary from day to day and component to component. One explanation could be the absorption and release of compounds by the argex grains or the biomass in the wetland. Since industrial wastewater was led through Wetland South for months, it is well possible that the grains were saturated with 4-/5-methyl-1H-benzotriazole and metformin, which is released in the communal wastewater. Metabolites like gabapentin lactam could be formed in the wetland. Small increases might be explained by differences in water quality between in- and outgoing water due to the retention time of 12 hours.

Round 3: December 2020/January 2021, AQUALYSIS, summary report in excel file.

The first two studies on the micropollutants did not consider the residence time of the water and the possible variation of concentrations during the day. The use of passive samplers has been discussed, but not chosen because the validation of this sampling technology for this specific project would consume more time and resources. It was decided to use automatic samplers with cooled compartments and collect 48hr-composites, where residence times were taken into account for start/stop of the 48h sampling periods.

From the list of analyzed components, the 1,2,3-benzotriazole and the sum of 4 and 5-methyl-1H-benzotriazole are of most interest. There is always some 1,2-3-benzotriazole present in the influent, even when MBR-only is fed to the wetland. It is hardly removed in the wetland and the biochar zone does not show any additional removal. The 4 and 5-methyl-1H-benzotriazole concentration is significant higher when a mix of Biox and MBR is fed. It is hardly removed in the wetland and the biochar zone does not show any additional removal. When MBR only is fed, the concentrations over the wetland are even increasing. This could indicate a build-up of these components till saturation and slow release if the concentrations in the feed are low. For all the other components in the list of analytes, the removal efficiencies vary from almost complete to no removal at all, where the biochar zone does not have any additional effect on the removal. More research will be needed to determine the removal mechanisms (adsorption and/or biodegradation) for the specific micropollutants.

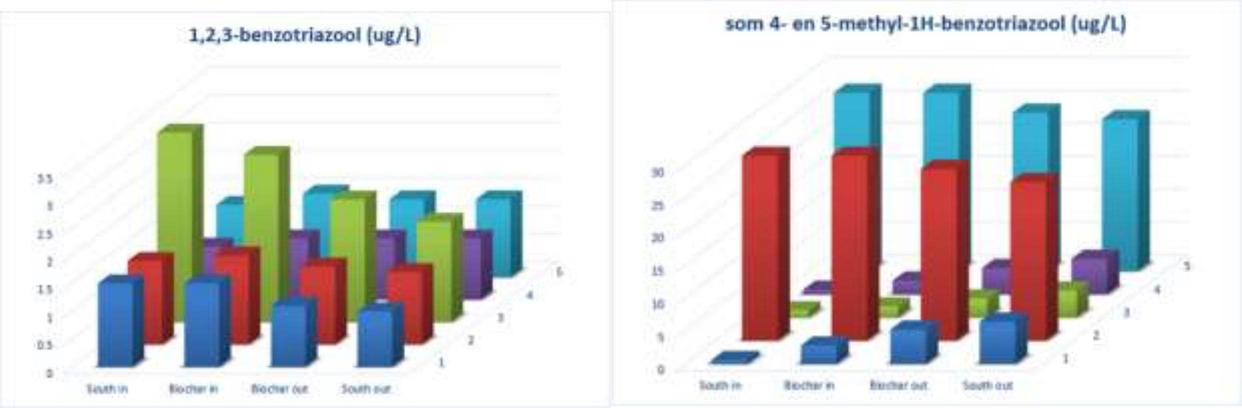

Figure 12: Round 3: example of micropollutant sampling results for benzotriazoles.

Round 4: May/June/July 2021, AQUALYSIS, summary report in excel file.

Composite samples were collected over 48h, where start-stop times were set to take in account the residence time. Time based composites (~50 ml aliquots every 15 minutes during 48h) were collected from following sampling points: Influent south, effluent south, UF-permeate and IEX-product were sampled over the course of 6 weeks. First four sampling events were done with a mixed feed to Wetland south. The last two sampling events were done with Biox effluent only. After the second sampling round, the aeration setting for zone 3 was changed from no aeration to setpoint 2-3 mg/L. From the list of analysed components, the 1,2,3-benzotriazole and the sum of 4 and 5-methyl-1H-benzotriazole are of most interest.

Both are present in the influent, significant higher concentrations when Biox only is fed to wetland south.
The benzotriazoles are hardly removed in the wetland and effluent concentrations are sometimes higher, possibly caused by varying concentrations in the influent combined with saturation effects.
UF and IEX are not removing the Benzotriazoles either.

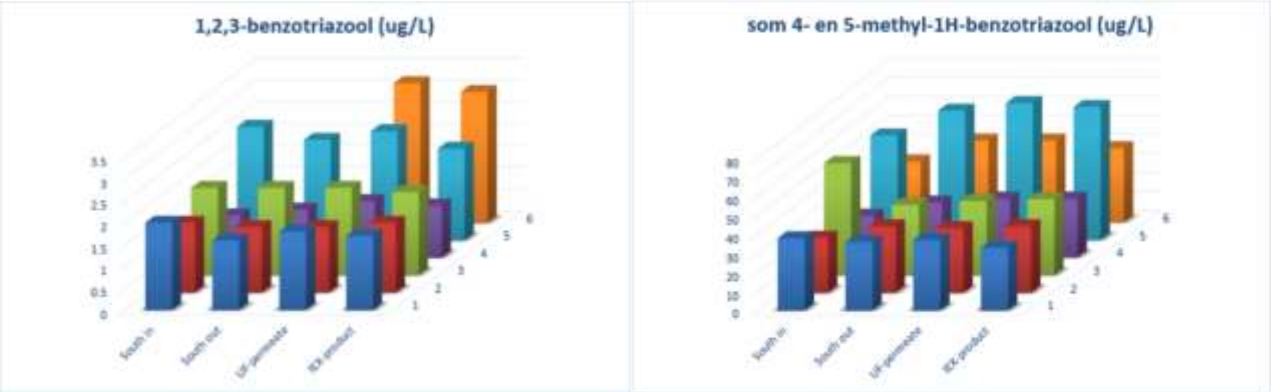

Figure 13: Round 4: example of micropollutant sampling results for benzotriazoles.

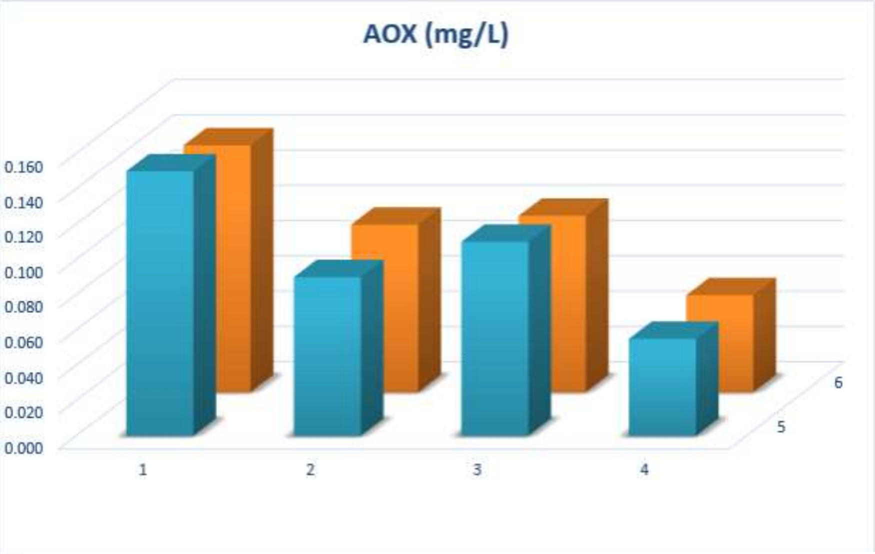

Figure 14: Results for AOX removal in constructed wetlands.

For all the other components in the list of analytes, the removal efficiencies vary from almost complete to no removal at all. For some components there is a slightly different behavior over the wetland compared to the earlier sampling round. More research will be needed to determine the removal mechanisms (adsorption and/or biodegradation) for the specific micropollutants.

For 2 of the sampling rounds in June (Biox only to influent), Adsorbable Organic Halogenide (AOX) concentrations are measured. AOX is a potential future discharge parameter for Cooling Tower blowdowns, so feedwater should be low on AOX. There is ~50 % removal over the wetland and IEX removes approximately another 25% of the AOX.

Dow specific components

Samples from the May/June/July study have been analysed at the Dow ADD -lab on Dow specific components (based on targeted and non-targeted screening of Dow internal wastewaters) Components that were identified with a certain level of confidence are: Triethyleneglcycol, Methylbenzotriazole, Benzotriazole, N,N-diethyl acetamide, N,N-diethyl propionamide, N,N-diethyl butyramide, Tetra propylene glycol. Although components were identified, the levels were lower than 10 μg/L. Also for these components, the removal efficiency over the wetlands and UF/IEX is low and not stable.

3.1.5 Leaching properties Argex & startup wetlands

Iron, Sulphate and Silica are identified as the main parameters that where leaching from Argex happened especially during the start-up phase and the first year of operation.

Iron

Iron was released especially in the first two months of operation. Average increase (based on monthly averages) was ~1 mg/L. For a start-up period of 2 months the total amount of released Iron can be calculated as ~15 kg/month for the two wetlands.

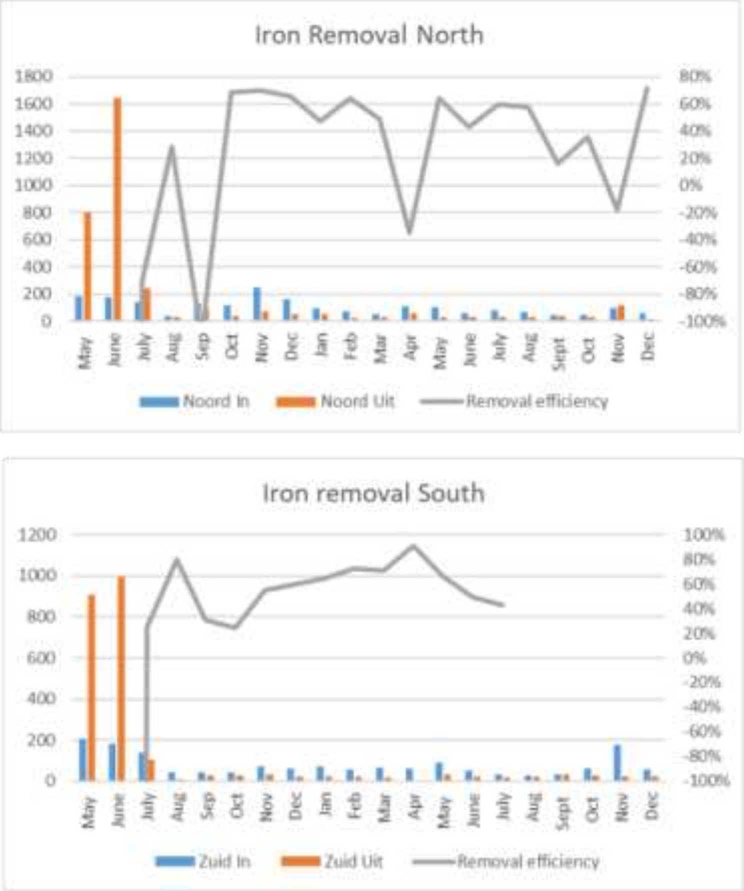

Figure 15: Iron in-out June 2019 – Dec. 2020

Sulphate

During the initial phase of the wetland, sulfate was leaching from the Argex substrate, which is a known phenomenon and related to the production process of the clay aggregates. Effluent concentrations on sulfate were significantly higher than influent concentrations especially in the first year of operation. Since early 2021 a more or less steady state is established where, depending on the influent concentrations, a minor adsorption or release can be observed. To calculate the amount of sulphate leached out from the ARGEX during start-up, the monthly averages on sulphate-in needs to be subtracted from the sulphate-out.

For the first year of operation (May 2019 – April 2020) the amount of SO_4 leached from both pilot wetlands can be estimated as 340 kg SO_4/month (Average difference 24 mg/L, 10 m³/hr per wetland).

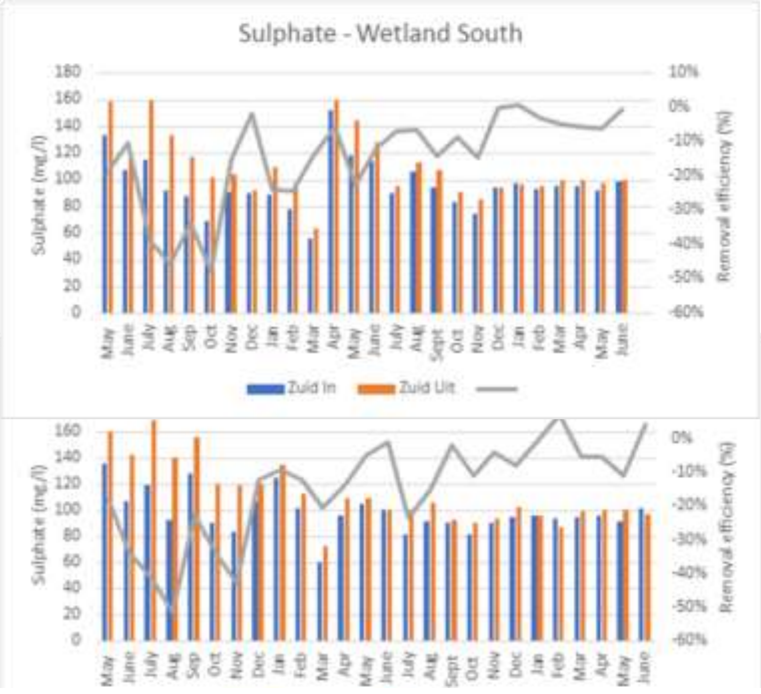

Figure 16: Sulphate in-out June 2019 – June 2021

Silica
During the first months of operations an increase in silica concentrations was observed over the wetlands. Presence of some silica is not considered to be a problem for the further treatment process.

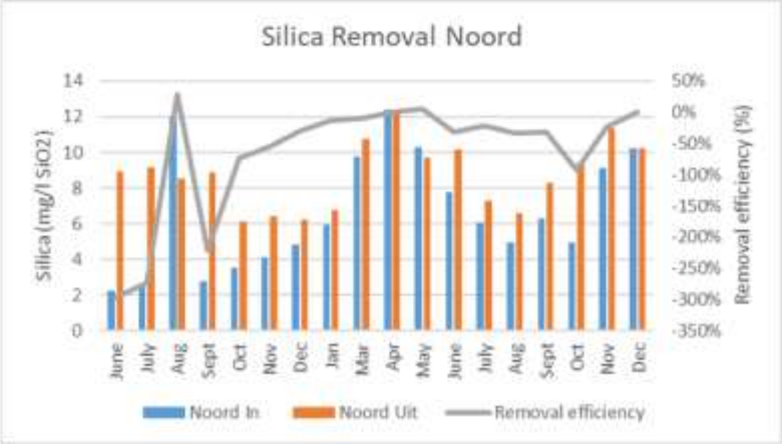

Figure 17: Silica in-out June 2019 – Dec. 2020

3.1.6 Reed harvesting & reed properties

During the year, part of the reed is mowed to maintain access to the Nitratax analyzer and the DO-probes. The mowed reed is left on the wetland. For the whole wetland, Rietland bvba advises a harvesting frequency of once per year to avoid any complications with larger trees clogging the wetland or perforating the liner. Harvesting is always done at the end of winter to minimize the water content of the harvested reed. Harvesting of all reed on both wetlands was done in February ’21. During harvest, reed was removed via a crane with mowing arm, also used to cut reed along ditches. Trees and shrubs were manually removed. The top layer of the ‘argex’-substrate was loose enough to easily remove any roots of trees and shrubs. Approximately 1.5 ton biomass was removed from both wetlands (2*350 m^2). Samples of the reed were collected and sent to Nutrilab for analyses and evaluation.

Figure 18: Reed harvesting in action after one year of operation.

If various quality specifications are met, reed can be used as roof cover. Nutrilab has performed analyses on these specific parameters[13]. Conclusion from Nutrilab can be summarized: Reed cannot be used for roof coverage. The high amount of leave material and high amount of nitrogen (low C/N ratio) will accelerate the decay process. Nitrogen content is extremely high, possibly caused by the nutrient rich water which flows through the wetlands. The high nitrogen content could be positive in case the reed is used in a digestor. For other applications, the amount of (heavy) metals in the reed can be an important parameter. Heavy metals in the reed can be a result of plant-uptake of elements by the plants. Therefore, Nutrilab has been asked to analyse for metals[12]. Results have not been checked against any limits for digestors or other applications.

Table 30: Heavy metals.

Metals & Minerals – Method	Resultaat	Reference values
Chroom (Cr) - ICP-OES - A6000 (klassieke ontsluiting)	< 1 mg/kg	E.g. for biomass for digestion?
Nikkel (Ni) - ICP-OES - A6000 (klassieke ontsluiting)	7,1 mg/kg	
Koper (Cu) - ICP-OES - A6000 (klassieke ontsluiting)	3,2 mg/kg	
Zink (Zn) - ICP-OES - A6000 (klassieke ontsluiting)	77 mg/kg	
Kwik (Hg) - Hg-analyser - A6180 (microwavedestructie)	0,010 mg/kg	
Arseen (As) - ICP-MS - A6300 (microwavedestructie)	0,071 mg/kg	
Cadmium (Cd) - ICP-MS - A6300 (microwavedestructie)	< 0,03 mg/kg	
Lood (Pb) - ICP-MS - A6300 (microwavedestructie)	0,33 mg/kg	

3.1.7 Clogging and suspended solids

One of the functions of a constructed wetland is the removal of Total Suspended Solids (TSS) from the influent. The amount of TSS in the MBR and BIOX flow has been low in the past two years of operation (see report Lies Hamelink), but TSS may increase if it is decided use effluent directly coming from the Terneuzen RWZI, instead of MBR treated water.

Clogging by suspended solids can result in partial flooding of the wetland because the hydraulic conductivity is too high to transport al the water subsurface. This would create 'short' cuts in retention, less effective treatment and possible odor issues.

Some flooding has been observed during operation, but different causes are assigned to these flooding's.

- Algae growth in the inlet zone
- Inlet flow higher than the design flow.
- Excessive biomass growth in the C-dosing zone

Algae growth

With respect to algae growth. Especially in the first months of 2021, the first half meter of the inlet zones were showing water on top of the Argex. For North, there were still some issues with the hydraulic conductivity as a result of the C-dosing experiments (excessive biomass growth in middle zone).

Due to continuous inflow of water, the inlet zone wax also showing a little bit lower Argex level. After some time, algae growth and biomass growth could be observed in the inlet zone, forming a slimy layer which made the situation even worse.

For wetland North a few different measures have been taken at different parts of the inlet zone.

- Reed removed in the first 50 cm
- Argex added to ensure that the influent water directly flows into the argex bed.
- Cover the first meter to protect the inlet zone from sunlight.

All three measures had a positive effect and are proposed measures in the addendum to the full scale design.

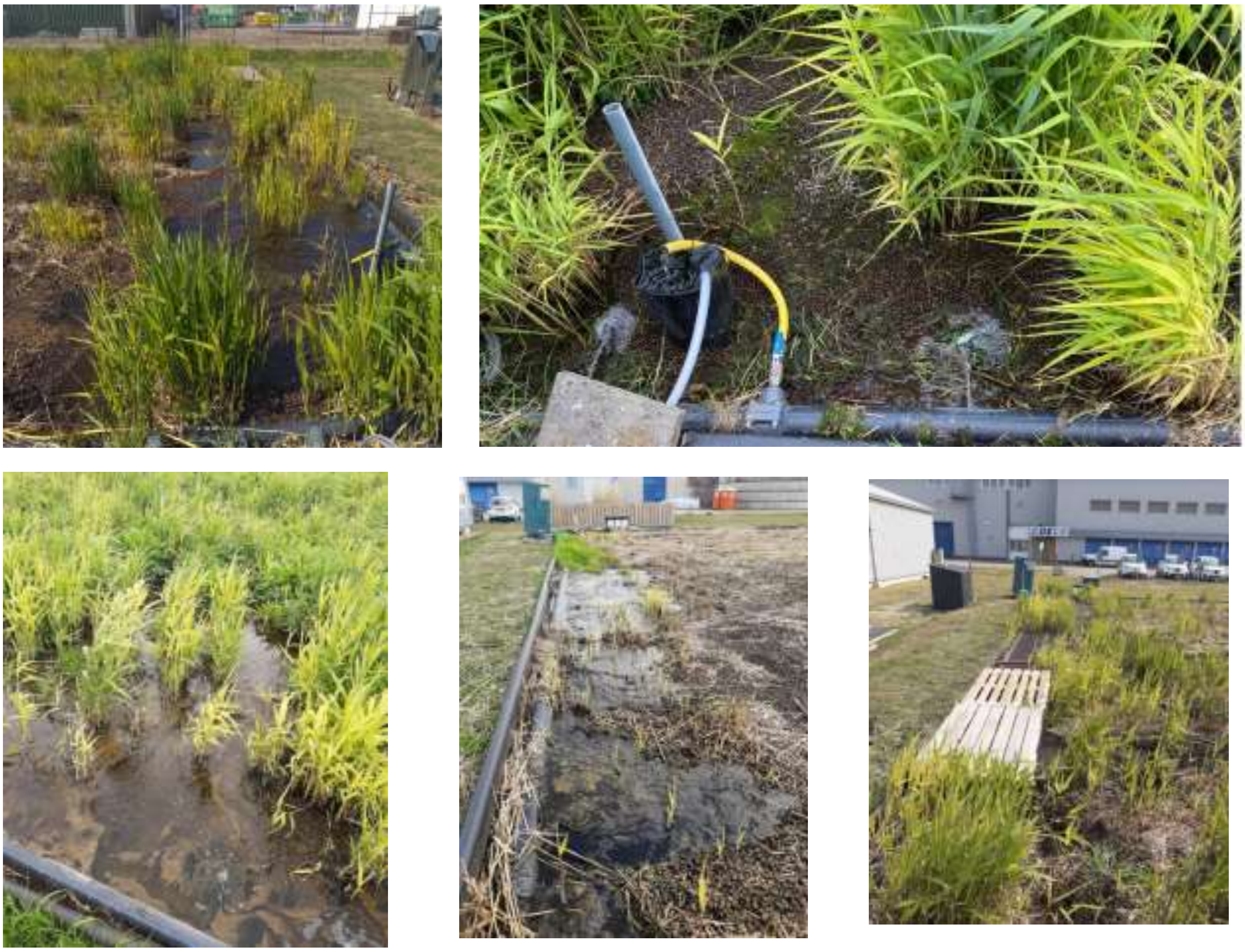

Figure 19: Illustrations of feedside of wetlands

Increased flow

In the period June-Aug 2021, the flow to Wetland North is gradually increased from 8 to 16 m3/hr. With higher flows (>14 m4/hr), some flooding of the first meter is observed. Water levels around the Nitratax are still 5-10 cm below the surface. If the flow is lowered to 'normal' levels, the water levels quickly drop and no water is visible on top of the inlet zone.

Excessive biomass growth

During the pilot, two experiments have been conducted to increase the denitrification by dosing an additional Carbon source in wetland North. In both experiments, the additional carbon caused issued with excessive biomass growth around the dosing zone. This caused flooding of the first zone and part of the second zone. A yellowish slime biomass was visible on top of the ARGEX. Even when the C-dosing was stopped, it a few weeks before the excess biomass was removed/dried-out. No C-dosing is planned in the full-scale wetland. So excessive biomass development is not expected.

3.1.8 Water balance

An aerated horizontal flow subsurface constructed wetland is much more efficient than a non-aerated system and due to the smaller footprint and the reed/substrate covered surface, less vulnerable for loss of water due to evaporation. Based on the information from Diederik Rousseau (mail March 16th, 2021) evaporation losses are negligible. There are different ways of calculating (E)TP, the most reliable one probably being the Penman-Monteith equation for calculating ETo (= reference = grass plot), and then converting in our case to *Phragmites* via a crop factor (FAO), see e.g. https://www.mdpi.com/2073-4441/11/10/2159/pdf. Results of calculations as well as measurements show in hot climates maximum loss about 2-3 cm/day; in Dutch climate losses of 1 cm/day during summer are expected. Obviously, evaporation losses will be much less in winter, in the order of 1 mm/day. An influent flow 240 m^3/day on 350 m^2 surface area. gives a hydraulic loading rate (HLR) of 240/350 = 0.685 m^3/m^2.day or in other words a HLR of 68.5 cm/day. So taking the most extreme case (3 cm/day loss), this would be a loss of 3/68.5 = 4.4%. In the Terneuzen case it would mean a loss of 1-2%

Rainwater will positively contribute to the water balance. Yearly rainwater sum for this region is 800 mm (= 800 L/m^2). On a wetland surface of 350 m^2, this means an additional amount of 280000 L or 280 m^3 on a hydraulic throughput of ~90000m^3 (~0.3%).

Based on these assumptions/calculations, there will be a net water loss between 1-2%.

3.1.9 Biofilm monitor experiments

Different options were considered to monitor the biofouling potential of the influent and effluent of the wetlands. "Biofouling potential" is a water quality parameter which is highly dependent on the equipment/technology used. The numbers generated with one instrument/technology can hardly be compared with other equipment or technology. To be able to compare the wetland performance with the 'base-case' technology (multimedia filtration + biologically activated carbon filter) it was decided to use the so-called the 'WLN-monitor'. Reference data technology gathered in the WLN-plant in Emmen is available for this monitoring technology.

A constant (metered) flow of water is pumped through a glass column filled with glass rings. With a laminar flow (no turbulence, no pressure shocks) a thin biofilm will build up on the surface of the glass rings. The glass tube and the sampling lines are protected from sunlight/daylight to prevent algae growth.
Within some boundaries, the biofilm build-up correlates with the exposure time/flow through the column. Every week two rings with a defined surface area are carefully removed from the column and transferred to a defined volume of clean water in a vial. In the lab (AQUALAB Zuid), the biofilm is transferred to the water phase by ultrasonic treatment (?) which is then analyzed for ATP content. Results are expressed in pg ATP/cm^2. Over time, the amount of ATP/cm^2 will increase because the build-up of the biofilm. Biofouling potential can also be calculated as biofilm growth rate in pg ATP/cm^2.day.

Figure 20: Biofilmmonitor WLN.

Two series of experiments are carried out:

1. June 11th to August 18th, 2020, mix feed 12 m³/hr with two wetlands in series.

Following aeration settings were used:

	Zone 1	Zone 2	Zone 3
Wetland North	aerated 2-2,5 mg/L	out	out
Wetland South	aerated 2-2.5mg/L	timed aeration (every 6hr, 0.5 hr oxygen on)	2-2.5mg/L

WLN monitors were installed on Influent North, Effluent North and Effluent south. For the effluents sampling, water was pumped from the effluent pits at the north west side of Wetland North. For the monitoring point at influent North, the glass tube and the glass rings were already heavily covered with biomass after one week.

Figure 21: Glass tubes of the different sampling locations after 1 and 10 weeks exposure

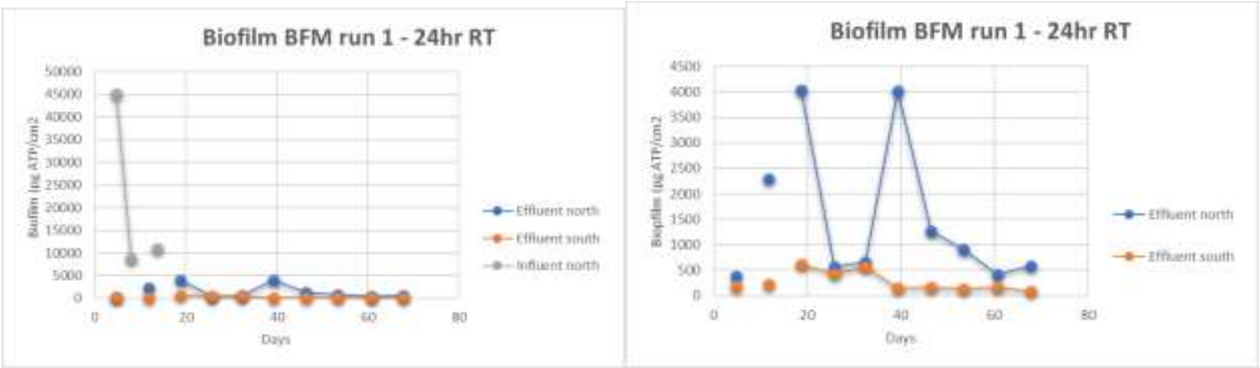

Figure 22: Biofilm formation on rings in pg ATP/cm² for all three sampling points (left graph) and effluent streams only (right graph).

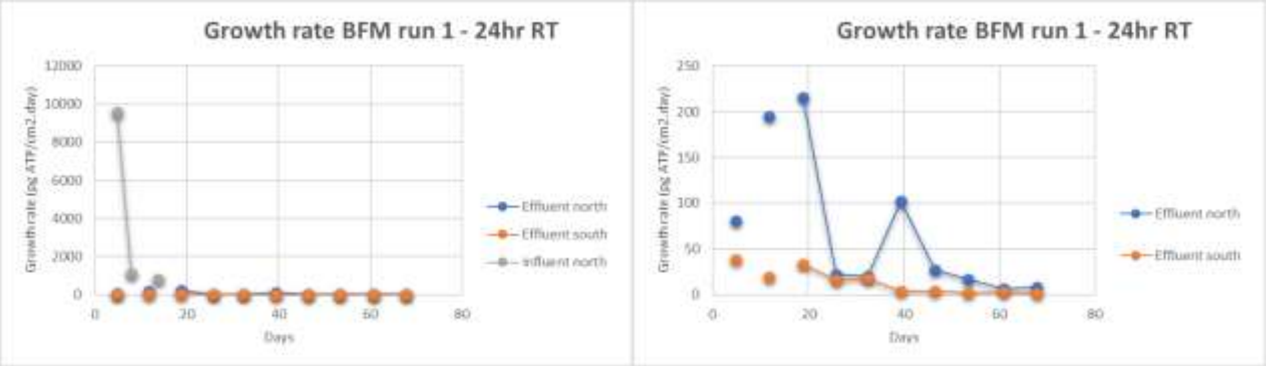

Figure 23: Biofilm growth rate in pg ATP/cm^2.day for all three sampling points (left graph) and effluent streams only (right graph)

The results for the biofilm development on the effluent monitors are not showing a significant increase over time. This results in in a downward trend in the growth rate. Possible explanation could be a very low amount of nutrients in the effluent streams preventing a growth of the biofilm or presence of low concentrations of growth/biofouling inhibiting components in the effluents of the wetland. The influent monitor could only be sampled 3 times. The excessive amount of biomass in the glass column and on the rings made it impossible to take out the rings in a representative way. Minor disturbances would remove significant parts of the fouling/biomass.
Based on these results it can be concluded that the wetlands do significantly reduce the biofouling potential. An additional 12h retention time reduces the biofouling potential even more.

2. December 3rd 2020 to Feb 9th, 2021, mix feed to wetland south, 10 m^3/hr.

Following aeration settings were used (zone 1 changed during the biofilm monitoring):

	Zone 1	Zone 2	Zone 3
Wetland South	aerated 2-2.5mg/L; 1-1.5mg/L and 0.5-1mg/L	Out Biochar passed	Out

The influent of wetland south was sampled in the field. For the monitoring of effluent south the WLN monitor was placed next to the UF-feed buffertank, which is continuously filled with effluent from the wetland effluent pit. An additional ÁQUALAB Zuid monitor was placed next to the one obtained from WLN.
The 4th monitor was placed next to the UF-permeate tank and fed with UF-permeate.

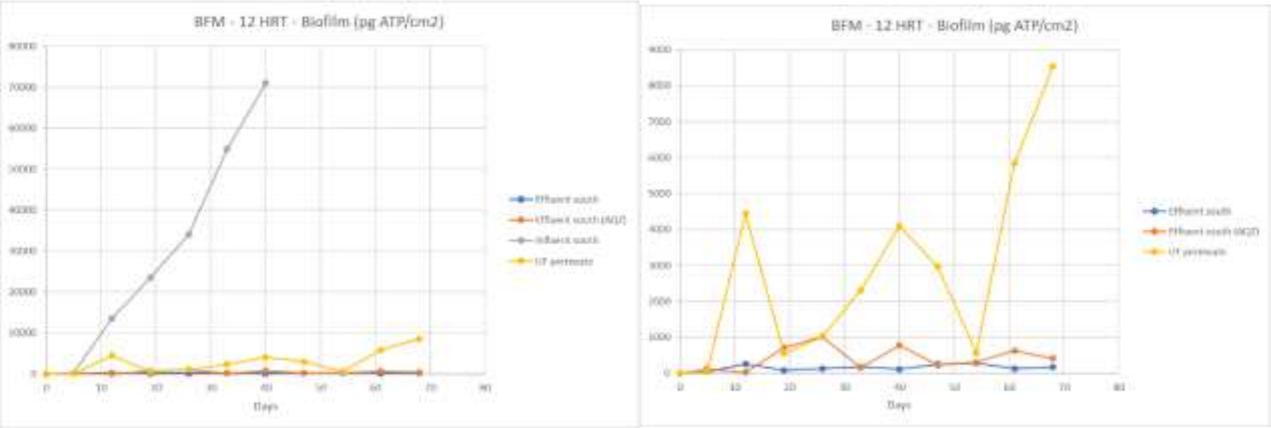

Figure 24: Biofilm formation on rings in pg ATP/cm^2 for all four sampling points (left graph) and effluent streams/UF permeate only (right graph).

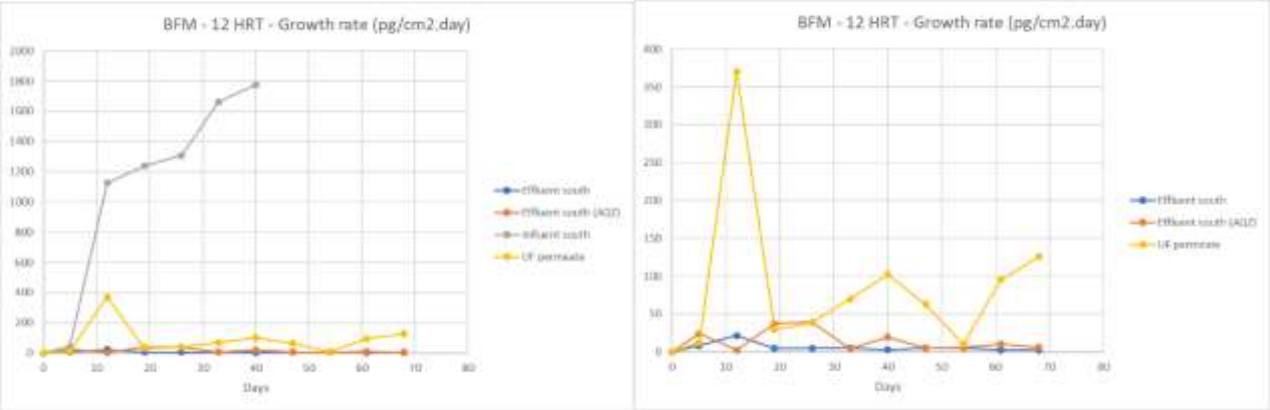

Figure 25: Biofilm growth rate in pg ATP/cm^2.day for all sampling points (left graph) and effluent streams and UF-permeate only (right graph).

The results of the second trial showed a more linear increase for the biofilm in the influent stream. Also the growth rate increased, possibly caused by additional fouling due to small biomass flocs from the influent stream. Both effluents showed a similar trend. The observed growth rate (~10 picogram/cm^2 .day) is significantly lower than the biofilm growth rate in the influent monitor. The UF-permeate values are significantly higher, most probably caused by additional bacteriological activity and presence of nutrients in the UF-permeate buffer tank. This is confirmed by ATP measurements directly in the water phase of these flows.

In an article on the Emmen case some graphs are presented on the biofilm formation before and after two Bacteriological Activated Carbon (BODAC) filters in series. Although conditions may be different, the results do give an idea on the reduction of biofilm formation over a wetland compared to the 'base-case' technology.

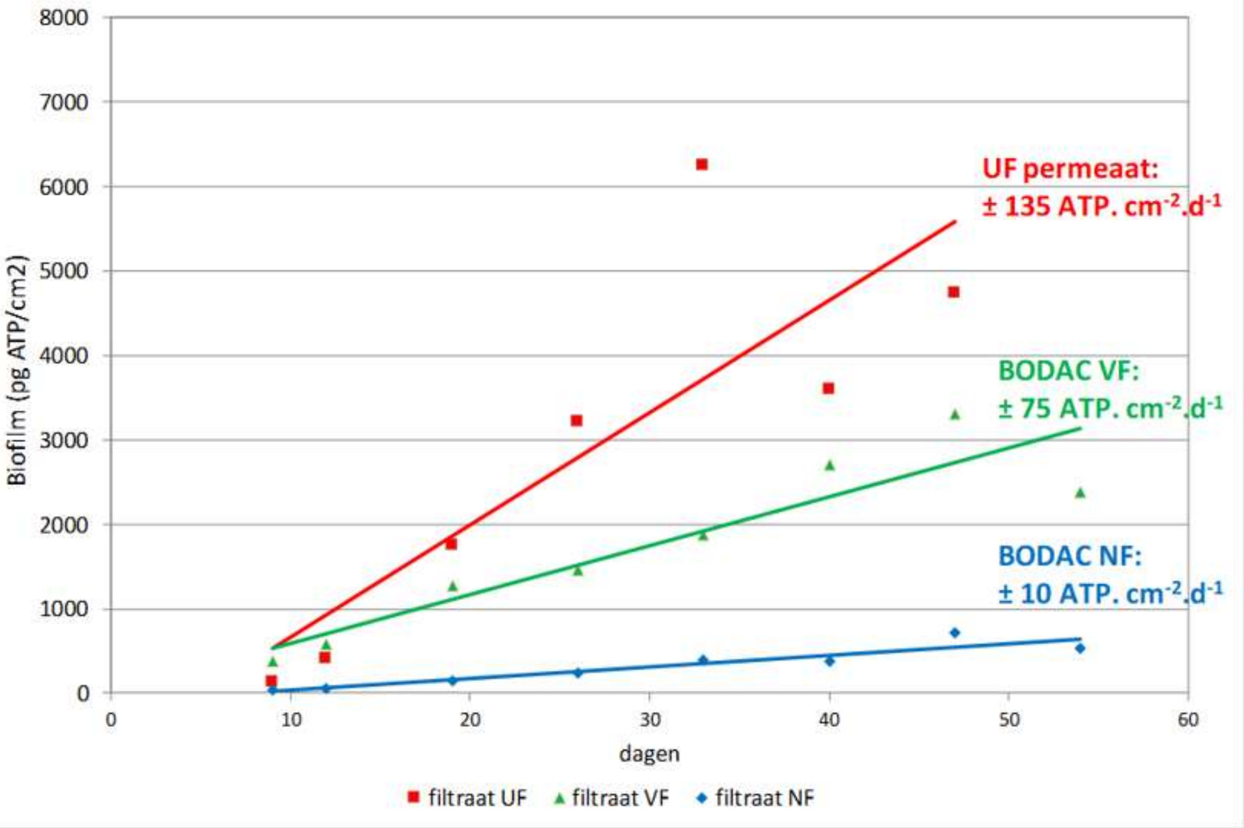

Figure 26: Results BACF WLN.

The growth rate after the second Bacteriological Activated Carbon filter is ~10 pg ATP/cm^2.day. This is comparable with the results obtained after the wetland – 12 h RT.
Ref: Geen biofouling op omgekeerde-osmosemembranen door voorzuivering met biologische actiefkoolfiltratie (h2owaternetwerk.nl)

3.1.10 Environmental aspects

Life cycle analysis (Evides)

A comparison has been made between the base case- and flagship scenario according to Evides-standards. The results have been summarized in a presentation made by Wilbert van den Broek. Though both scenario's appeared comparable, some key information was still missing to make a fair comparison. For example, the reuse of Argex has not yet been taken into account.

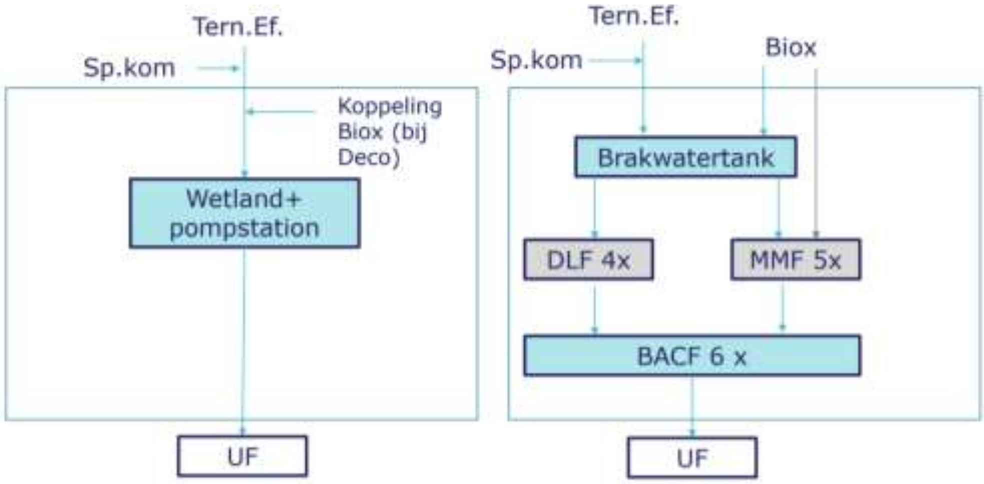

Figure 27: Overview comparison LCA base case- and flagship scenario.

Valuing nature (Dow)

As part of the Valuing nature goals, Dow has set NPV goals on projects that will 'value' nature. A calculation model has been developed to score the impact on air/water/land. Together with the Dow team and evaluation is planned to assess the wetland project.

Biodiversity scan Sweco

Sweco is performing biodiversity assessments on the Dow site. A screening study will performed on how to maximize the positive effects of a wetland and surrounding green infrastructure on the biodiversity in the area. Expected delivery of this report by Sweco in November '21.

End-of-life Argex granules

For the LCA calculations and in view of circularity, it is important to know if the LECA can be re-used after the expected lifetime of a constructed wetland. There is only limited information available on conventional wetlands filled with LECA that have been in operation for 20 years. According Tauw and Argex, there is a market for used LECA, but it needs to fulfill certain environmental and product quality criteria. According Dutch regulations, it needs to comply to 'Besluit en Regeling bodemkwaliteit' before it can be re-used as 'bouwstof'. On May 11th 2021 samples have been taken from the two wetlands using an 'edelman' sampler and a riverside sampler. Root material and remainders of reed and plants have been removed from the samples. All subsamples, taken from the middle of wetland north and south, zone 1,2 and 3 and at three depths (-10cm to -40cm, -40cm to -70cm and -70cm to -90cm) have been combined and sent to Eurofins

Barneveld for analyses. The results from the analysis are summarized in the report made by Tauw[14] and the results of the leaching tests do not give rise to concerns to (re)use the Argex as building material.

In addition to the leaching test, compositional analyses have been performed. Organic matter, which is also important for re-use was <0.7%. Monoaromatic hydrocarbons, Polycyclic hydrocarbons, PCB’s and mineral oil were all below detection limit which indicates that these pollutants do not build-up in the LECA. Various metals were detected in the LECA itself, but most of the analyzed metals will originate from the clay itself as leaching tests did not show relevant leaching of ‘adsorbed’ metals.

On June 17th samples from wetland south have been collected. Two samples have been sent to Argex for analyses: Wetland south, zone 1: 40 cm below water level and Wetland south, zone 3: 20-20 cm below water level. Results have been discussed in a meeting with Argex on August 19th and reports have been received. The main conclusion was that the average grain size does not comply with the original specification of Argex AR 8/16-340 material because too many smaller particles (<8 mm) were present. However, it would fit the AR 6/16 specifications. Presence of smaller grains may be due to the way the Argex is blown into the wetland during construction.

3.2 Ultrafiltration

This chapter describes the performance of the UF for the experiments with- and without the wetlands.

3.2.1 Performance of UF without wetlands as pretreatment

The results of the described tests can be seen in the figures below. Figure 28 depicts the permeability of the UF per feed water source and Figure 29 depicts the permeability of the UF over time since the start of the research. Figure 6 shows that the performance of the UF is dependent on the feedwater source, but more on the pre-treatment. Direct treatment with especially MBR and the Mix resulted in an unstable permeability. Direct treatment with Biox resulted in several stable tests, but there was not enough data from this period to make full conclusions. The instability of direct treatment is also clearly visible in Figure 29. The down-ward trend in permeability is clear, even after placing new membranes (March 2020). A CIP was done in September 2019 and September 2020, both CIP’s did not result in a clear increase in permeability indicating that the fouling on the membranes could not be removed easily. Several tests with draining all permeate tanks (backwash water) resulted in a reduction of pressures, which could indicate that the system is mostly prone to biological fouling by either biological growth in the permeate and / or growth on the membrane surface. The growth could be severe enough that it cannot be removed by CEB’s and / or CIP’s. The hypothesis that biological growth in the water caused the fouling of the UF membranes was confirmed after switching to the pre-treatment with the constructed wetlands. As indicated, a CIP was done in September 2020, before the switch to the constructed wetlands. At the beginning of the first test with the CW, the permeability was low. After a few days of operation the permeability started to increase and eventually resulted in a permeability close to clean membrane permeability, CEB’s were done as before within the first week of running with the CW. It seemed the biological growth in the system was destabilized by the new feed-water, most likely due to the lack of nutrients that are removed by the wetland. As a result the system got cleaner each cycle (after each BW and each CEB).

Treating effluent of the MBR and the Biox directly with UF was considered the worst-case scenario for the operation of the UF. In the base-case scenario the UF feedwater would be pre-treated by DLF and BACF, which will probably resolve the issue of biological growth.

3.2.2 Performance of UF with the constructed wetland as pretreatment

As mentioned earlier the permeability of the UF started to increase after the switch to the CW as pre-treatment (October 2020, see Figure 29). From this point the performance of the UF is very stable, with little variation in permeability. The UF does however react to changes in the wetland. Often, a switch from a mixed feed-water source to only Biox results in a temporarily lower permeability. After a few cycles however, the permeability will restore. Similar patterns can be seen when suddenly the aeration of the wetland is stopped, and therefore the availability of oxygen. It is believed that sudden changes in the

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[14] Dow/Evides, inventariserend onderzoek bouwstoffen regeling. Report: L001-1281743RTA-V01-los-NL

wetland (like a changing feed-water source or a sudden lack of oxygen) results to some shock to the biology in the wetland causing bacteria to flush out which effects the permeability of the UF (not confirmed by measurement). A long term test (several weeks) without aeration in the wetland did result in a slightly lower but overall stable permeability, meaning the UF can cope without aeration in the wetland. The lack of oxygen does not cause irreversible fouling to the membranes.

3.2.3 Performance of the UF with the constructed wetland as pre-treatment and brine reuse

Since the start (March 2021) with RO brine as backwash water for the UF (used during backwash and CEB's) the permeability of the UF didn't change much. In fact, the average permeability of the UF tends to be a bit higher (not significant) with the brine reuse than without (see Figure 29). This might be due to the disinfecting effect of salts in the RO brine. RO brine can be used successfully to backwash the UF, within the research period no negative effect on the performance of the UF could be found. Another benefit is that the RO brine doesn't contain scalants like calcium and magnesium (when pre-treated by IX softening), that can cause precipitants with caustic CEB's. The normally used UF permeate is not softened.

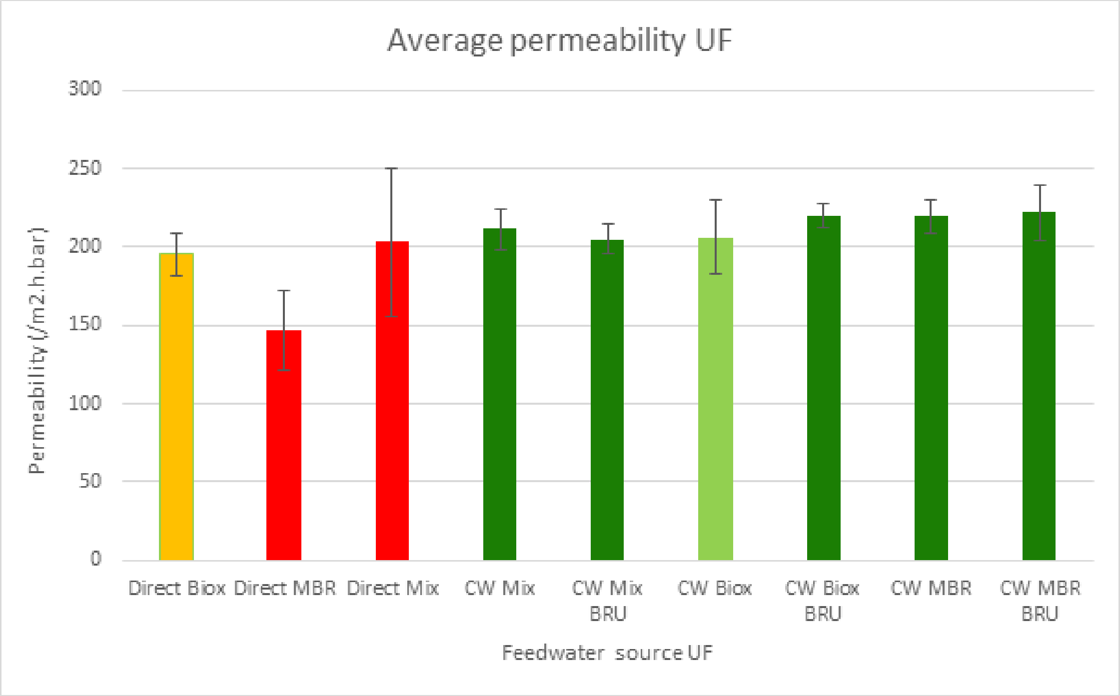

Figure 28: Average permeability of the UF with the different feedwater sources. Red bars indicate an unstable performance, orange bars indicate a doubtful performance (towards unstable), dark green bars indicate a stable performance and light green bars indicate a stable performance that needs some more caution. With each bar the feed water source is indicated. The text BRU means that RO brine was used to backwash the UF.

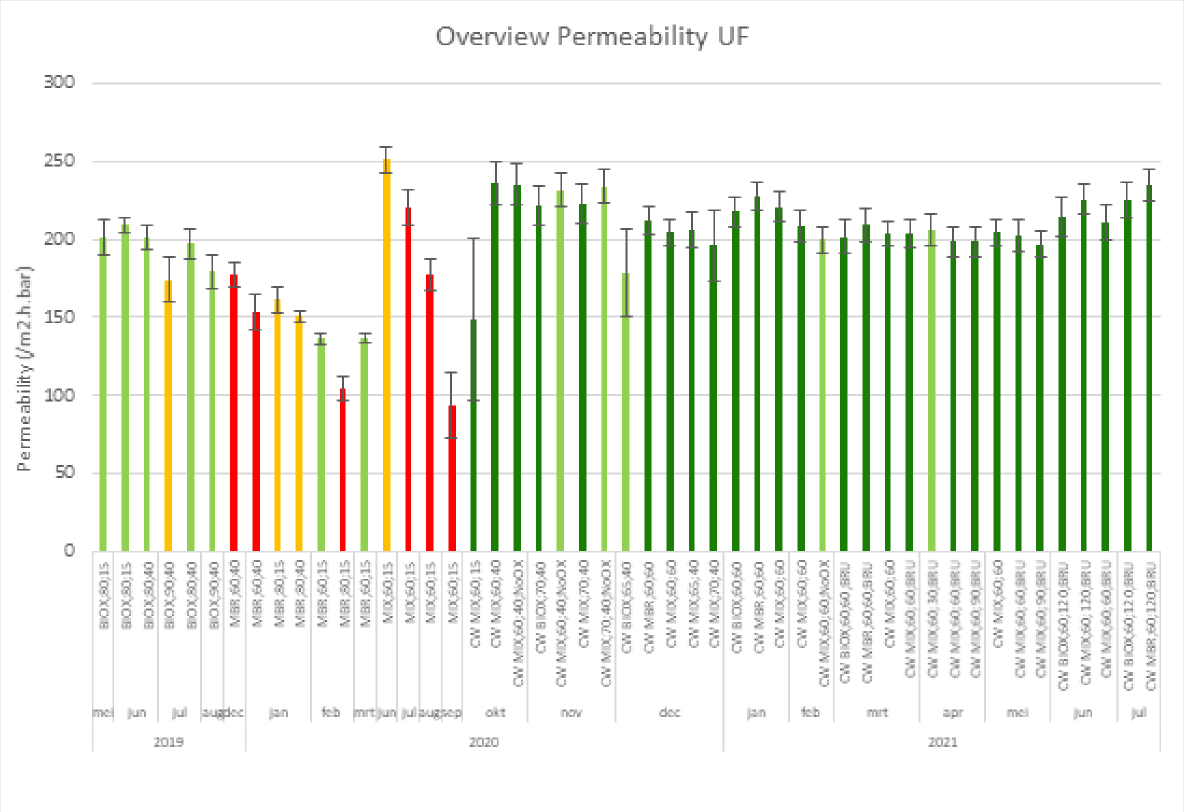

Figure 29: Overview of the average permeability of the UF for each test over time. Red bars indicate an unstable performance, orange bars indicate a doubtful performance (towards unstable), dark green bars indicate a stable performance and light green bars indicate a stable performance that needs some more caution. With each bar the feed water source, flux and filtration time is indicated. The text BRU means that RO brine was used to backwash the UF. The text NoOX means that the wetland was not aerated.

Room for improvement

A constructed wetland as pre-treatment for the UF proved to be very successful. Filtrations of 60 minutes with hardly any permeability decrease since October 2020 indicate that there is room for improvement, meaning that the limits of the UF system have not been found in the tested configuration. In the current situation (August 2021) the UF is running on a flux of 60lmh and a filtration time of 2 hours with the same result (no decrease in permeability). Next steps to be tested:

- Reduce the amounts of CEB's (including crash-testing, how long can the system do without).
- Increase filtration time (also including crash-testing).
- Increase flux (could not be increased due to limits of the system and the demand of the other pilots).

3.3 Ion-exchange (softener-scavenger)

3.3.1 Main results HPR8300 WAC resin, Amberlite SCAV4 Cl (SCAV4) and Amberlite IRA458 Cl (IRA458) SBA resins experiments with IX1 pilot (7)

OC and regeneration ratio of the WAC resin HPR8300

The OC of the HPR8300 WAC resin was tested at two regeneration ratios. Based on DuPont Tech Fact 177-03729 (8) the recommended range of the regeneration ratio for WAC resin with HCl is 105-110%, while with NaOH is 110-160%. The lowest recommended regeneration ratio (105%) was compared to a higher regeneration ratio (135%) for both chemicals. The resulted OC as well as information about the feed water quality of the experiments can be seen in Table 31. It was found that independently from the regeneration ratio an OC of about 3.80 eq/LR (80% of the TVC) can be achieved. The program WAVE was used in an effort to verify the achieved OC, but different OCs were obtained by changing the dimensions of the WAC columns (e.g. from IX1 to IX2 or full scale). Moreover, WAVE does not offer the option for a counter current regeneration. Therefore, it is considered vital to further research the OC of the HPR8300 WAC in cased of the mixed stream with IX2 pilot experiments.

Table 31: WAC resin regeneration levels results (7)

Regeneration ratio (%)	105	135
Feed Ca^{2+} concentration (mg/L)	58.85	
Feed Mg^{2+} concentration (mg/L)	9.15	
Feed total hardness (meq/L)	3.7	
Batch 1 – OC (H^+ form, eq/L_R)	3.96	3.89
Batch 1 – OC (H^+ form, eq/L_R)	3.56	3.80
Batch 1 – OC (H^+ form, eq/L_R)	4.02	3.97
Batch 1 – OC (H^+ form, eq/L_R)	3.69	3.60
Average – OC (H^+ form, eq/L_R)	3.81	3.81
SD – OC (H^+ form, eq/L_R)	0.22	0.16

Performance of the SCAV4 and IRA458 SBA resins

Experiments with the SCAV4 and IRA458 in different regeneration levels in order to calculate the OC of the resins took place. The resulted OC capacities for the two resins at the different regeneration levels can be seen in Figure . The operational capacity calculated at the different regeneration levels for SCAV4 ranged from 36 to 46% of its total capacity. The operational capacity of IRA458 was 35 to 42 % of its total capacity. The total capacity of IRA458 is higher than that of SCAV4. Consequently, the operational capacities achieved at each regeneration levels for IRA458 were higher than that for SCAV4.

In column operation, resins are not totally regenerated and part of the resin bed remains exhausted. When higher amount of NaCl is dosed during regeneration, more Cl^- ions are available to regenerate the SBA resins and a smaller part of the resin bed remains exhausted. Therefore, a greater number of exchange sites is available for ion exchange to take place in the following production. As expected, based on the above statement, a higher regeneration level resulted in an increase of the OC. Achieving this at the same chemical dosage the IRA458 is able to produce with a lower stoichiometry. Taking into account the amount of chemicals required in each case and the subsequent OC achieved, it was concluded that a regeneration level as low as 80 gr NaCl/L_R is feasible and the possibility of even lower levels should be investigated.

It must be noted that the OC was calculated based on the removal of HCO_3^-, NO_3^-, HPO_4^{2-}-P, SO_4^{2-} and TOC. Specifically, the calculation were based on the removal presented in Figure . The contribution of TOC removal to the operational capacity was calculated based on the excess Cl^- found in the product water that is not explained by the removal of the other anions. In later phase of the research, it was decided for practical reason to exclude TOC and HCO_3^- removal from the calculations of the OC. The corrected OC values for no TOC and HCO_3^- removal are given in Figure . An interesting note is that from the OC used for only anions removal a 30% can be attributed to HCO_3^- removal.

Two important noted about the conditions of these experiments follow:

- The SBA resin regeneration was upward (counter current) and the resin beds during regeneration were operated in a non-packed mode.
- The pH in inlet of the SBA columns ranged from 8.5 to 9.5, the contribution of HPO_4^{2-} was above 90% and the contribution of $H_2PO_4^-$ was below 10%.

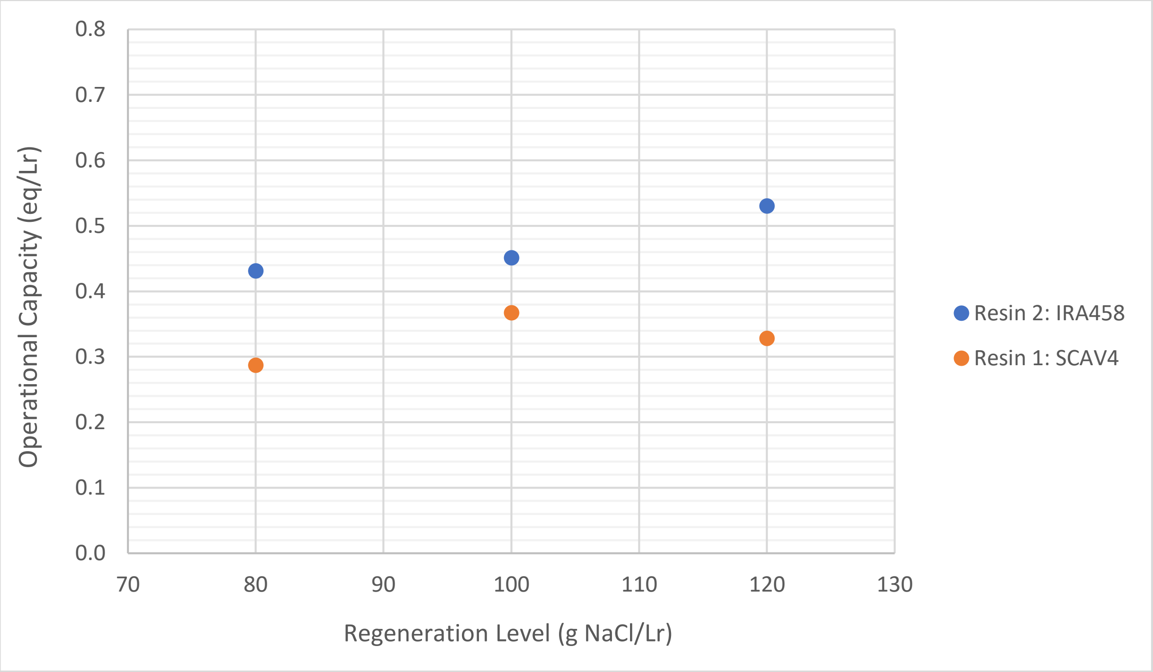

Figure 30: OC of SCAV4 and IRA458 at the different regeneration levels (7)

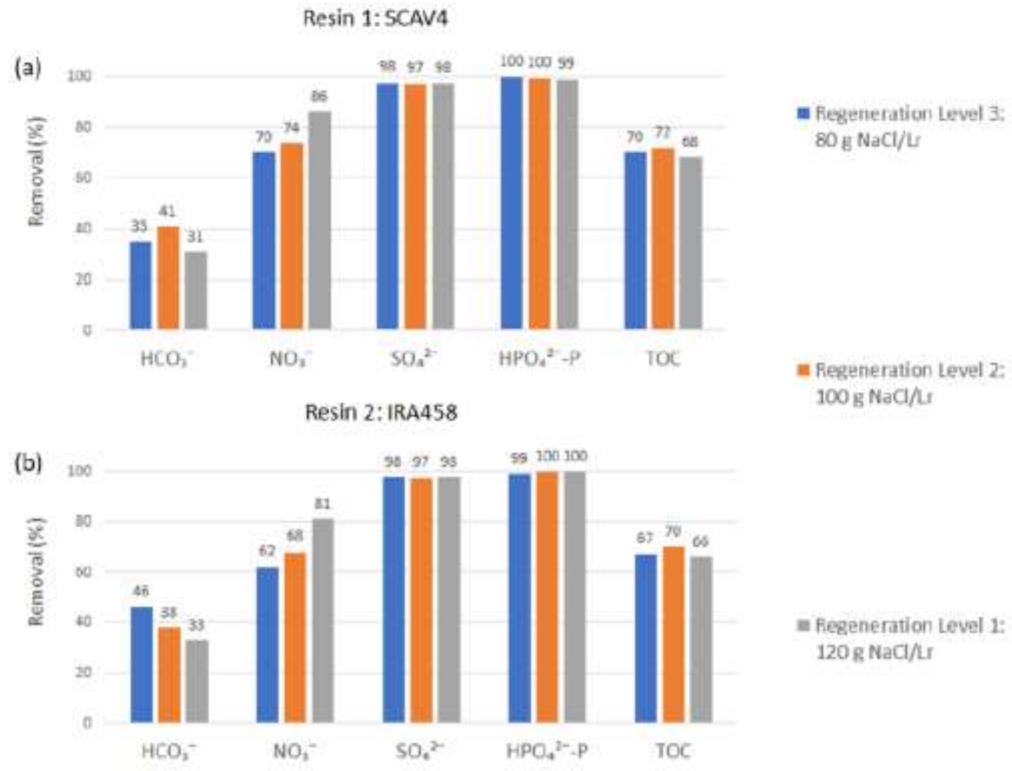

Figure 31: Removal of anion and TOC at the three regeneration levels by (a) resin 1 (SCAV4) and (b) resin 2 (IRA458) (7)

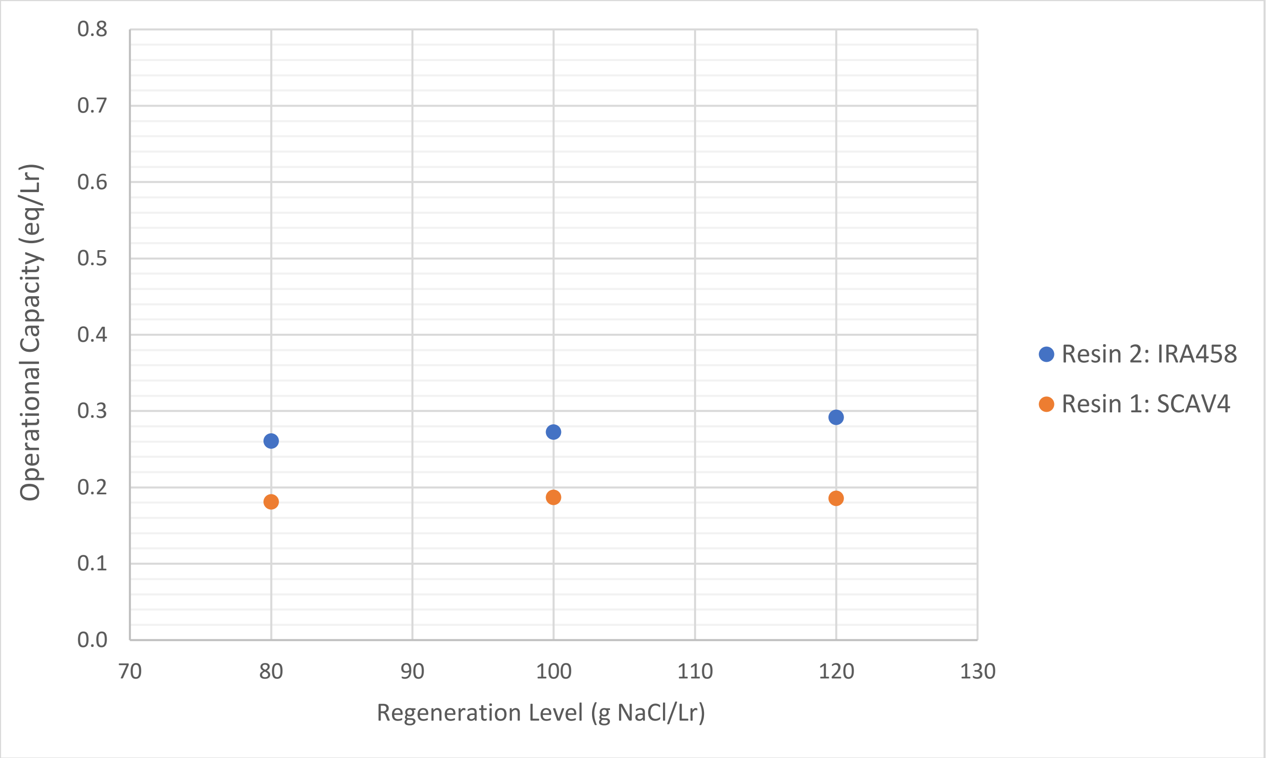

Figure 32: Corrected OC for no TOC and HCO_3^- removal of SCAV4 and IRA458 at the different regeneration levels (7)

Selectivity Order Experiments for SCAV4 and IRA458 SBA resins

The anions selectivity order for both SCAV4 and IRA458 was found to be the following:
$HCO_3^- < NO_3^- < HPO_4^{2-} < SO_4^{2-}$

Moreover, from the selectivity order experiments it was observed that HPO_4^{2-}-P breakthrough starts at the point where NO_3^- in product water reached its highest concentration (greater than its feed concentration) as it can be seen in Figure . Therefore, it was concluded that high removal of SO_4^{2-} and HPO_4^{2-}-P (above 97%) can be achieved up to the point where product NO_3^- concentration reaches its feed concentration. Thus, a higher amount of water (throughput) can be produced with the same water quality regarding SO_4^{2-} and HPO_4^{2-}-P.

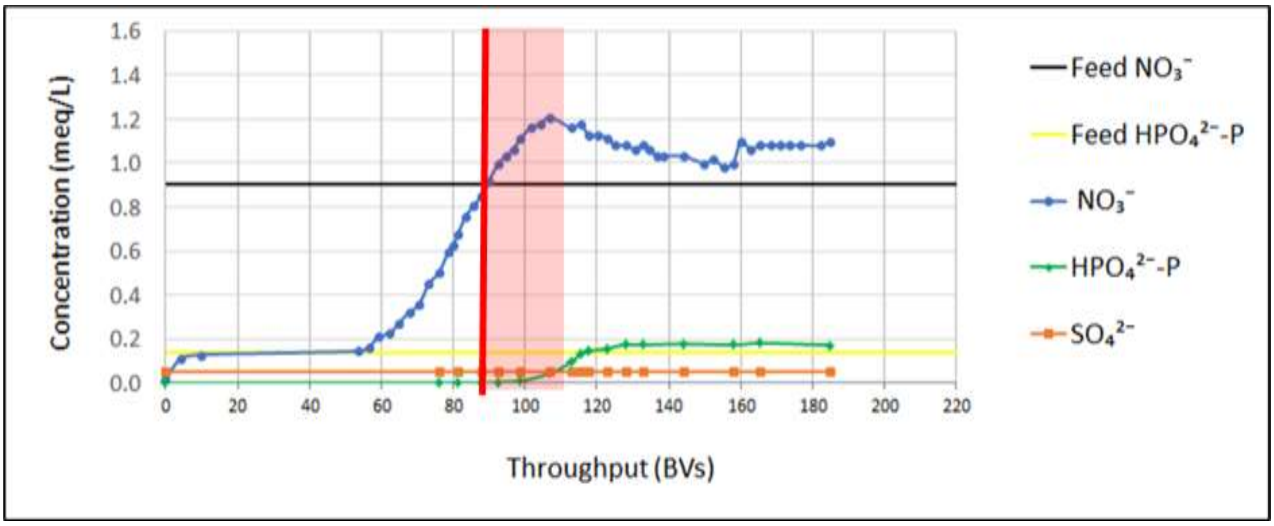

Figure 33: Anion selectivity order experiment for SCAV4 (7)

Bio-growth potential test on product samples of SCAV4 and IRA458 SBA resins

A bio-growth potential test was performed in a UF permeate sample, which is the IX feed, and in two product water samples; (i) Product 1 after treatment with HPR8300 (WAC) and SCAV4 (SBA) and (ii) Product 2 after treatment with HPR8300 (WAC) and IRA458 (SBA). The pretreatment of MBR effluent (after UF treatment) with IX1 treatment consisting of a WAC resin and in series either one of the two tested SBA resins resulted in P, N and C removal of approximately 99%, 83% and 70%, respectively. The removal of nutrients led to a substantial reduction in the bacterial growth potential of above 90% (Figure 34). A switch in the growth-limiting nutrient from C to P was caused by IX treatment with either SBA resin. Bio-growth test results also suggest that both SBA resins removed a considerable fraction of AOC. Both P limitation and AOC reduction lead to lower biofouling expectation in RO modules using feed water pretreated with UF and IX1 with either SBA resin compared to RO modules fed with only UF pretreated water.

Moreover, another interesting observation was that in the product samples with either SBA resin the nitrogen (N) content (due to NO_3^- concentrations) was in excess for bacterial growth compared to C and P content as it was also verified from the growth-limiting nutrient results. In microbial biomass, the C:N:P molar ratio is 100:20:1.7 (9), which corresponds to a mass ratio of 23:5:1. The C:N:P ratio for the three water samples is given in Table 32. Thus, it was concluded that having even higher NO_3^- content in IX product samples is acceptable, since N is already in excess and more N won't increase further the bacterial growth potential.

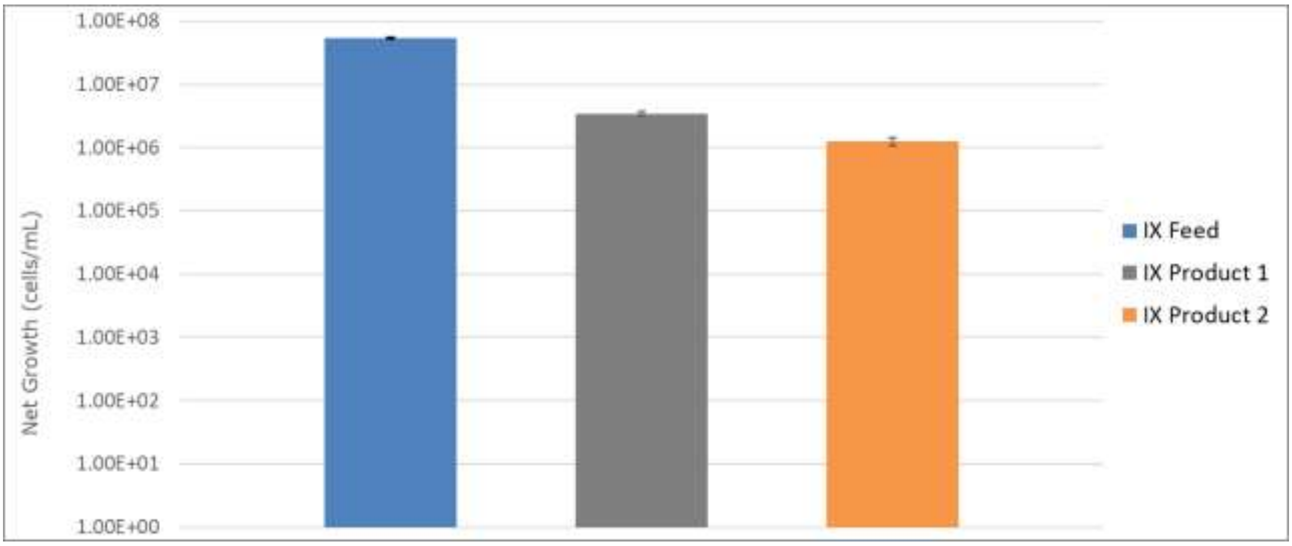

Figure 34: Net cell growth of blank samples IX Feed, Product 1 (SCAV4) and Product 2 (IRA458). The error bars indicate the error on triplicate samples (graph in logarithmic scale) (7)

Table 32: C: N: P mass ratio from bio-growth test samples (7)

	IX Feed/ UF permeate	Product 1 (SCAV4)	Product 2 (IRA458)
C (mg/L)	7.2	2.1	2.2
N (mg/L)	14.3	2.2	2.5
P (mg/L)	1.85	0.01	0.01
C:N:P	4:8:1	210:220:1	220:250:1

Scaling potential software runs on product samples of SCAV4 and IRA458 SBA resins

The scaling potential that was assessed with PHREEQC 3 and Avista Ci software of the IX1 product water with either SBA resin was low for several scalant types. Among them was calcium phosphate, which was found to have high scaling potential in RO feed without IX treatment either with or without anti-scalant dosing. Still, anti-scalant dosing was found to might be required after IX treatment with either SBA resin due to the high scaling potential of some silica and iron-based minerals.

3.3.2 Results from the HPR9100 and HPR9000 SBA resins research with IX1

In Figure 35 the results of the selectivity order experiments for HPR9100 and HPR9000 SBA resins are given. The NO_3^- baseline leakage is equal to an average value of 17 mg/L for HPR9100 and 20 mg/L for HPR9000. An important difference in the behaviour of those two resins compared to SCAV4 and IRA458 is that HPO_4^{2-}-P is detected in the product samples from an early point in the production. Specifically, after only 40BVs and 16BVs for HPR9100 and HPR9000, respectively. Also, in case of HPR9100 HPO_4^{2-}-P in product reach its feed concentration before NO_3^-. SO_4^{2-} was in all product samples below detection limit (<5 mg/L). The pattern that HPO_4^{2-}-P concentration in the product water samples follows resembles more a baseline leakage rather than a breakthrough curve (not a sharp line). This result was unexpected for these two resins.

The OC achieved by the two resins until NO_3^- in product to be equal to NO_3^- in feed was 0.6 eq/L_R and 0.5 eq/L_R for HPR9100 and HPR9000, respectively. These OC were higher than those achieved by SCAV4 and IRA458 at the same regeneration level. No matter that it was decided not to proceed with further research for the selection of those two resins for the full scale due to firstly the early HPO_4^{2-}-P breakthrough noted and secondly the time limitation at that moment until the end of the brackish water line pilot study (different priorities rose).

Figure 35: Selectivity order experiments for the HPR9100 and HPR9000 SBA resins

3.3.3 Results from IX2 research with SCAV4

Seven runs took place in total with SCAV4 used as the SBA resin in IX2 pilot. An extra trial run was initially performed (named Run 0). In Table 33 a brief description and the main results of all runs are summarized. The OC calculated for each batch performed in Runs 1 to 7 are given in Figure 36. In this figure it can also be seen the average values from each run, the source of the feed water and some comments about the regeneration settings. The product water quality (significant parameters) and the subsequent removals for Runs 1 to 7 are given in Table 34.

Table 33: SCAV4 Runs with IX2 - Summary

Run	Dates	Details	Main Result
Run 0: Trial Run	24/12/20 to 19/01/21	1. Feed: 28% mixed stream 50/50 BIOX&MBR and 72% only MBR 2. WAC regeneration: 150% HCl and 130%NaOH over passed equivalents 3. SBA regeneration with 80 g NaCl/L_R 4. Start from 12h and gradually increase production hours to reach NO_3^- breakthrough (no P in product)	**Gradual increase till 0.498** eq/ L_R based on 100% removal of SO_4^{2-} , 100% removal HPO_4^{2-} and 36% removal NO_3^{2-}
Run 1: 80 gr NaCl/L_R & no P in product	19/01/21 to 03/02/21	1. Feed: 100% mixed stream 50/50 BIOX&MBR 2. WAC regeneration: 150% HCl and 130%NaOH over passed equivalents 3. SBA regeneration with 80 g NaCl/L_R 4. Rule: NO_3- in product ≈ Feed and HPO_4^{2-} < 0.05 mg/L (no P in product)	**OC = 0.502** eq/L_R based on 100% removal of SO_4^{2-}, 100% removal HPO_4^{2-} and 36% removal NO_3^{2-}
Run 2: 60 gr NaCl/L_R & till P in product equal to P in feed	08/02/21 to 16/03/21	1. Feed: 100% mixed stream 50/50 BIOX&MBR 2. WAC regeneration: 140% HCl and 120%NaOH over passed equivalents 3. SBA regeneration with 60 g NaCl/L_R 4. Rule: HPO_4^{2-}-P in product ≈ HPO_4^{2-}-P in feed ≈ 0.6 mg/L	**OC = 0.492** eq/L_R [15] based on 100% removal of SO_4^{2-}, 30% removal HPO_4^{2-} and 4% removal NO_3^{2-}
Run 3: 60 gr NaCl/L_R & till P in product equal to P in feed & simultaneously NaOH and NaCl dosing	16/03/21 to 24/03/21	1. Feed: 35% mixed stream 50/50 BIOX&MBR and 65% only MBR 2. WAC regeneration: 240% HCl and 400% Na+ from NaOH&NaCl over passed equivalents 3. SBA regeneration with 60 g NaCl/L_R 4. Simultaneously dosing of NaOH and NaCl 5. Rule: HPO_4^{2-}-P in product ≈ HPO_4^{2-}-P in feed ≈ 0.6 mg/L	**OC = 0.288** eq/L_R based on 100% removal of SO_4^{2-}, 65% removal HPO_4^{2-} and 24% removal NO_3^{2-}
Run 4 (restore capacity): Intense regenerations of SBA columns with HCl – and back to separate dosing of NaOH and NaCl (60 gr NaCl/L_R) & till phosphorus in product equal to phosphorus in feed	24/03/21 to 12/04/21	1. Feed: 100% mixed stream 50/50 BIOX&MBR 2. WAC regeneration: 156% HCl and 132%NaOH over passed equivalents 3. SBA regeneration with 60 g NaCl/L_R 4. Rule: HPO_4^{2-}-P in product ≈ HPO_4^{2-}-P in feed ≈ 0.6 mg/L	**OC = 0.430** eq/L_R based on 100% removal of SO_4^{2-}, 70% removal HPO_4^{2-} and 14.4% removal NO_3^{2-}
Run 5: Brine Re-use with 60 gr NaCl/L_R & till P in product equal to P in feed/2	13/04/21-22/04/21	1. Feed: 100% mixed stream 50/50 BIOX&MBR 2. WAC regeneration: 200% HCl and 170%NaOH over passed equivalents 3. SBA regeneration with 60 g NaCl/L_R 4. Rule: HPO_4^{2-}-P in product ≈ HPO_4^{2-}-P in feed/ 2 ≈ 0.3 mg/L 5. All regeneration steps expect of prewash with RO concentrate	**OC = 0.427** eq/L_R based on 100% removal of SO_4^{2-}, 77% removal HPO_4^{2-} and 7% removal NO_3^{2-}

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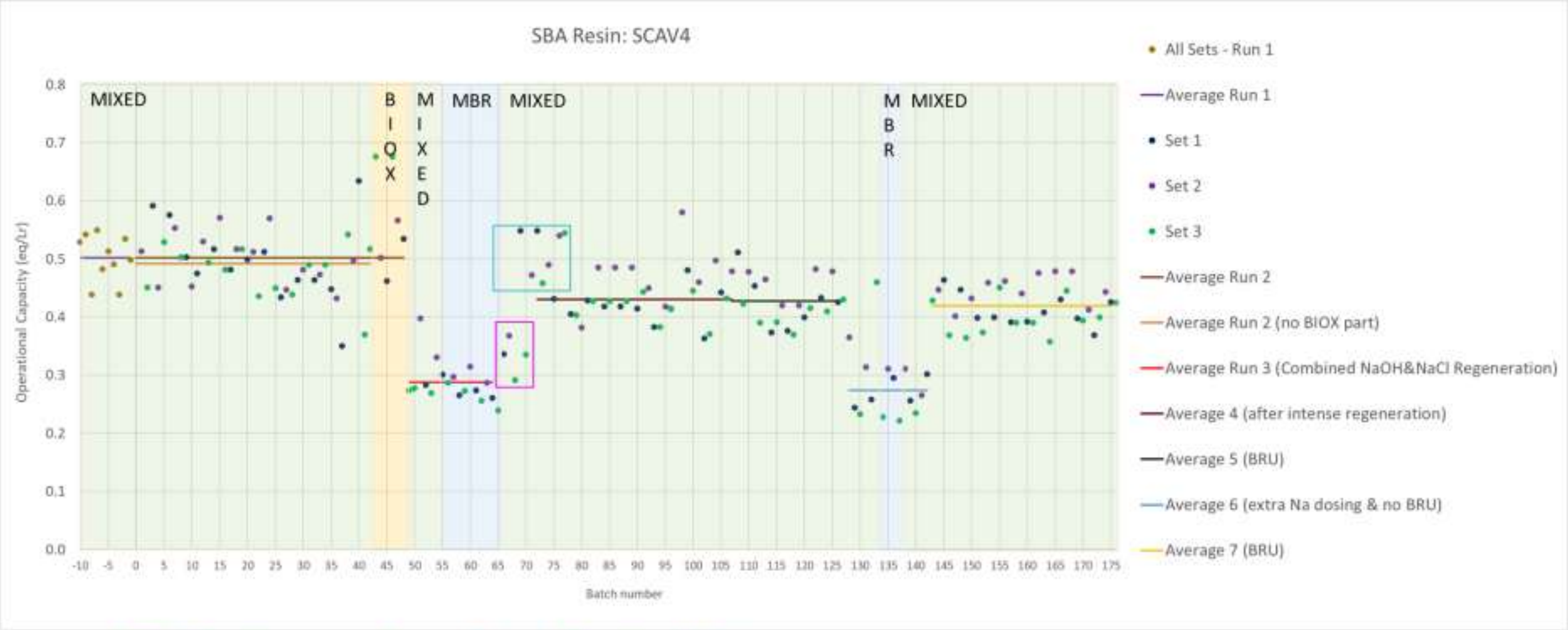
[15] The OC based on the average of the batched from Run 2 without the batched when only BIOX was feed (green highlighted region).

Run 6: recap run – no brine re-use & till P in product equal to P in feed/2	22/04/21-30/04/21	1. Feed: 70% mixed stream 50/50 BIOX&MBR and 30% only MBR 2. WAC regeneration: 200% HCl and 400%NaOH over passed equivalents 3. SBA regeneration with 60 g NaCl/L_R 4. Rule: HPO_4^{2-}-P in product ≈ HPO_4^{2-}-P in feed/2 ≈ 0.3 mg/L	**OC = 0.274** eq/L_R based on 100% removal of SO_4^{2-}, 45% removal HPO_4^{2-} and 0% removal NO_3^{2-}
Run 7: Brine Re-use with 60 gr NaCl/L_R & till P in product equal to P in feed/2	30/04/21-17/05/21	1. Feed: 100% mixed stream 50/50 BIOX&MBR 2. 1st half WAC regeneration: 170% HCl and 144%NaOH over passed equivalents 3. 2nd half (after 10/05/21): 170% HCl and 70%NaOH over passed equivalents 4. SBA regeneration with 60 g NaCl/L_R 5. Rule: HPO_4^{2-}-P in product ≈ HPO_4^{2-}-P in feed/2 ≈ 0.3 mg/L 6. All regeneration steps expect of prewash with RO concentrate	**OC = 0.419** eq/L_R based on 100% removal of SO_4^{2-}, 85% removal HPO_4^{2-} and 9% removal NO_3^{2-}



→ After double regeneration and stop of combined dosing

→ After intense HCl regeneration

Figure 36: OC achieved in different batches in Runs 1 to 7 with SCAV4 in IX2

Table 34: Product water quality and removals for Runs 1 to 7 with SCAV4 in IX2

		Run 1		Run 2		Run 3		Run 4		Run 5		Run 7	
Parameter	**Unit**	**Product (mg/L)**	**Removal (%)**	**Product (mg/L)**	**Removal (%)**	**Product (mg/L)**	**Removal (%)**	**Product (mg/L)**	**Removal (%)**	**Product (mg/L)**	**Removal (%)**	**Product (mg/L)**	**Removal (%)**
TOC	mg/L C	2.5	70	3	65	3.5	60	3	65	3.5	65	3	65
SO_4^{2-}	mg/L	<5	98	<5	98	<5	98	<5	98	<5	98	< 5	98
NO_3^-	mg/L	20	36	24	4	26	24	20	14.4	17	7	21	9
HPO_4^{2-}-P	mg/L P	< 0.05	98	0.4	30	0.3	65	0.3	70	0.1	77	0.1	85
Ca^{2+}	mg/L	<0.2	99	<0.2	99	<0.2	99	<0.2	99	<0.2	99	<0.2	99
Mg^{2+}	mg/L	<0.1	99	<0.1	99	<0.1	99	<0.1	99	<0.1	99	<0.1	99

Run 0: SCAV4 Trial runs

Run 0 started with a fixed production of 12h, which based on the average feed water quality results in an OC for the SBA resin of 0.25 eq/L_R. This value was the expected OC for SCAV4 based on results from IX1 research that took place during Gkoutzamani's thesis research (sub-chapter 3.3.1). Running with this OC the NO_3^- concentration in product water was low. The rule for the operation of IX was "to stop the production at the point where NO_3^- in IX2 product is approximately equal to the NO_3^- in IX2 feed". By following this rule it was possible within few days of operation to gradually increase the OC from 0.25 eq/Lr to 0.498 eq/Lr. Some differences between the operation of IX1 and IX2, in which the difference in the OC achieved with IX1 and IX2 can be attributed, were the following:

1) In the experiments with IX1 pilot the SBA resin beds during regeneration were not packed, while in IX2 were packed.
2) In IX2 the NaOH dosing passed only through the WAC column, while in IX1 was passing first through the WAC column and then trough the SBA column.
3) The feed water during IX1 experiments took place with only MBR effluent pre-treated with UF and during IX2 experiments the feed of the brackish water line was for the 28% of the research period the mixed MBR and BIOX 50/50 stream and 72% only MBR
4) The pH after the WAC columns and before the SBA columns was between 8.5-9.5 in case of IX1 pilot experiments, while in experiments with IX2 that pH was 6.5 to 8.5.

Run 1: SCAV4 80 gr NaCl/Lr & no P in product

During Run 1, the three sets were running with a fixed production time of about 30h, since the software required to control the production length based on the product water quality was not available from the start of the experimental period. 9 batches per set took place (27 in total). The NO_3^- concentration in the product water was monitored with an online analyzer and checked to be at any case smaller or equal the NO_3^- concentration in feed water. The feed water through the whole research period was the mixed stream 50/50 MBR & BIOX. The regeneration of the SCAV4 SBA resins took place with 80g NaCl/L_R and the achieved OC was 0.502 eq/L_R based on full removal of SO_4^{2-} and HPO_4^{2-} and 36% removal of NO_3^- feed equivalents (Table 34). TOC was removed by 70% and it was not taken into account for the OC calculations.

Run 2: SCAV4 60 gr NaCl/Lr & till P in product equal approximately to P in feed

In Run 2, the required forward for the control of the production length based on the product water quality (either NO_3^- or HPO_4^{2-}P concentration) was available. The regeneration of the SCAV4 SBA resins took place with 60 gr NaCl/Lr. Both the NO_3^- and HPO_4^{2-}-P concentrations in the product water were monitored with two online analyzers. The rule to stop the production and send the longest running set (of the 2 or potential 3 in production) for regeneration was set at the point where the HPO_4^{2-}-P concentration in product was equal to the HPO_4^{2-}-P concentration in the feed water. That concertation was about 0.6 mg P /L.

The feed water throughout Run 2 was mostly the mixed stream 50/50 MBR & BIOX, except of the last 4 days where MBR was not available and the feed water of the brackish water line was only BIOX (green highlighted area in **Fout! Verwijzingsbron niet gevonden.**). If all batches performed including those with only BIOX as feed are taken into account then the average OC achieved is at 0.501 eq/Lr (brown average line in **Fout! Verwijzingsbron niet gevonden.**) based on full removal of SO_4^{2-} and 30% removal of HPO_4^{2-} and 4% removal of NO_3^- feed equivalents. An increase of the OC was noted when the feed water was changed from the mixed to only BIOX (this effect will be discussed in paragraph 3.3.4). If the BIOX period is not taken into account and the OC is based only on the mixed stream batches, the resulted average OC is 0.492 eq/Lr based on full removal of SO_4^{2-} and 30% removal of HPO_4^{2-} and 4% removal of NO_3^- feed equivalents.

The main anion and TOC removal can be seen in Table 34. It must be noted that in this run over exhaustion of the SBA resin was noted, since the HPO_4^{2-}-P in the product was often noted to be much higher than that in the feed. As a result, SO_4^{2-} leakage was noted in the IX2 product samples. This problem was caused by a delay in the regeneration patterns; at a point where a set needed to regenerate it was not possible because another set was in regeneration and the regeneration of two sets simultaneously was not possible because firstly there was only one available regeneration station and secondly because at any time two sets needed to be at least in production to provide sufficient amount of water for the ROs. It is considered that if the regeneration patterns are closely monitored and the setpoint "to stop production at product P = feed P/2" is followed, the SO_4^{2-} leakage issue won't occur in full scale.

Comparing Run 1 and Run 2, it can be seen that a 25% reduction in chemical dosing (NaCl) from Run 1 to Run 2 resulted in merely 2% reduction in the achieved OC. Moreover, by keep on producing in Run 2 "till P in product equal to P in feed" the product water quality was deteriorated, since the NO_3^- removal was reduced from 36 to 4% and the HPO_4^{2-}-P removal was reduced from 98% to 30% in Run 1 and Run 2, respectively. This deterioration in the product water quality as far as NO_3^- is concerned is acceptable. The reduction in HPO_4^{2-}-P removal however is not, and it should be maintained in higher level as mentioned in the previous paragraph in order to also avoid SO_4^{2-} leakage in product water at any time.

Run 3: SCAV4 60 gr NaCl/Lr & till P in product equal approximately to P in feed & simultaneous dosing & Run 4 (restore capacity): Intense regenerations of SBA columns with HCl – and back to separate dosing of NaOH and NaCl (60 gr NaCl/Lr) & till phosphorus in product equal to phosphorus in feed

In Run 3 the combined dosing of NaOH and NaCl through both the WAC and SBA columns in series was tried. The same chemical amount with Run 2 for both was used in the combined dosing. The combined dosing was expected to be beneficial for the following reasons:

1) Less water would be required for the regeneration, since the steps of NaOH and NaCl would happen with the same amount of water.
2) Less time would be required for the regeneration, since the steps of NaOH and NaCl would happen simultaneously.
3) More equivalents will be available for the regeneration of the SBA (Cl^- similar with previous run and extra OH^- ions) thus the same or a bit higher OC was expected
4) The pH during the regeneration of the SBA would be higher; In higher pH, TOC solubility is higher and thus it was expected that it would be better removed from the resin during regeneration and thereby on the long term delay the negative impact of organic fouling of the resins.

However, an unexpected result was noted; The OC was down by 41.5% from 0.492 eq/L_R in Run 2 to 0.288 eq/L_R in Run 3. A further decrease of the OC was noted throughout Run 3 when the feed water was changed from the mixed to only MBR (this effect will be discussed in paragraph 3.3.4).

The pH pattern during an example regeneration in Run 2 is given in Figure . The water's pH before the SBA column is never below 7 and after the SBA columns during NaCl regeneration starts from 8.3 and rises to 9.5 once the NaCl flow starts. However, in Run 3 a different pH pattern is noted (Figure). Specifically, the HCl dosing takes place only in WAC column. Then, the displacement of excess HCl takes place in the WAC column. And the pH by the end of the HCl displacement is at 3.8 and the EC above detection limit. This means that the HCl displacement was not long enough. During Run 1 and 2 that was not a problem because further displacement was achieved during the NaOH dosing (plug flow) by-passing the SBA column. But, in Run 3 the further displacement is achieved during the combined dosing of NaOH and NaCl and this flow passes as well through the SBA column resulting on a pH pattern before the SBA columns as follows:

1) Initially the displacement of remaining HCl regenerant at a pH that starts at 3.9 and increases to 5.9 that contains the Ca^{2+} and Mg^{2+} ions and residual HCl.
2) Later on the displacement of NaOH and NaCl regenerant with a pH that is dropping to 3.8. Thus, the water entering the SBA columns contains some Cl^-, OH^-, Na^+ and H^+. The H^+ are reacting with the OH^- forming water molecules. But, the content of H^+ are more than that of OH^-, since more Na^+ equivalents that replace the H^+ were dosed (from the NaOH and NaCl) compared to the OH^- equivalents dosed (from just NaOH). This is verified by the pH drop.

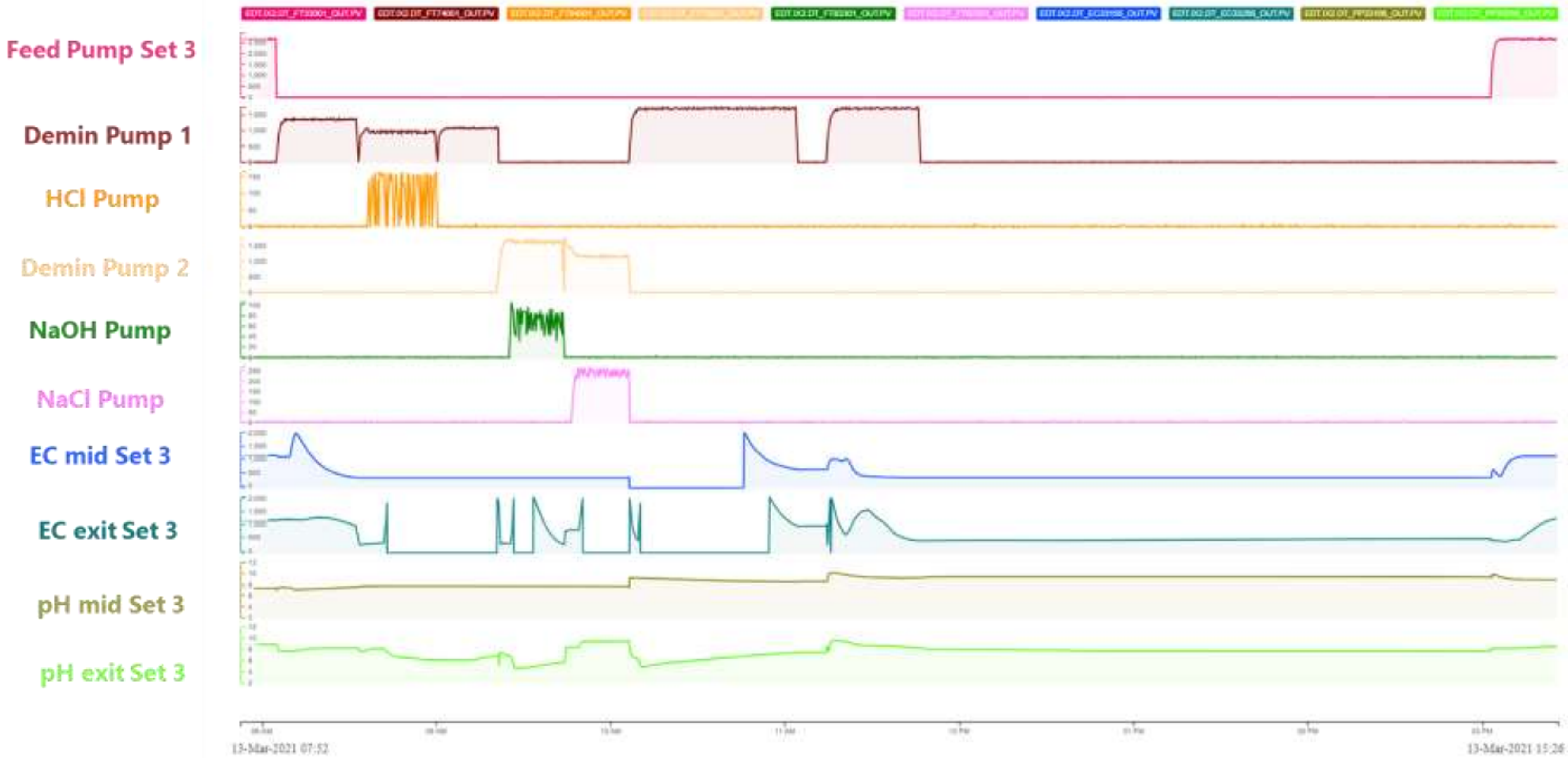


Figure 37: pH patterns during regeneration in Run 2

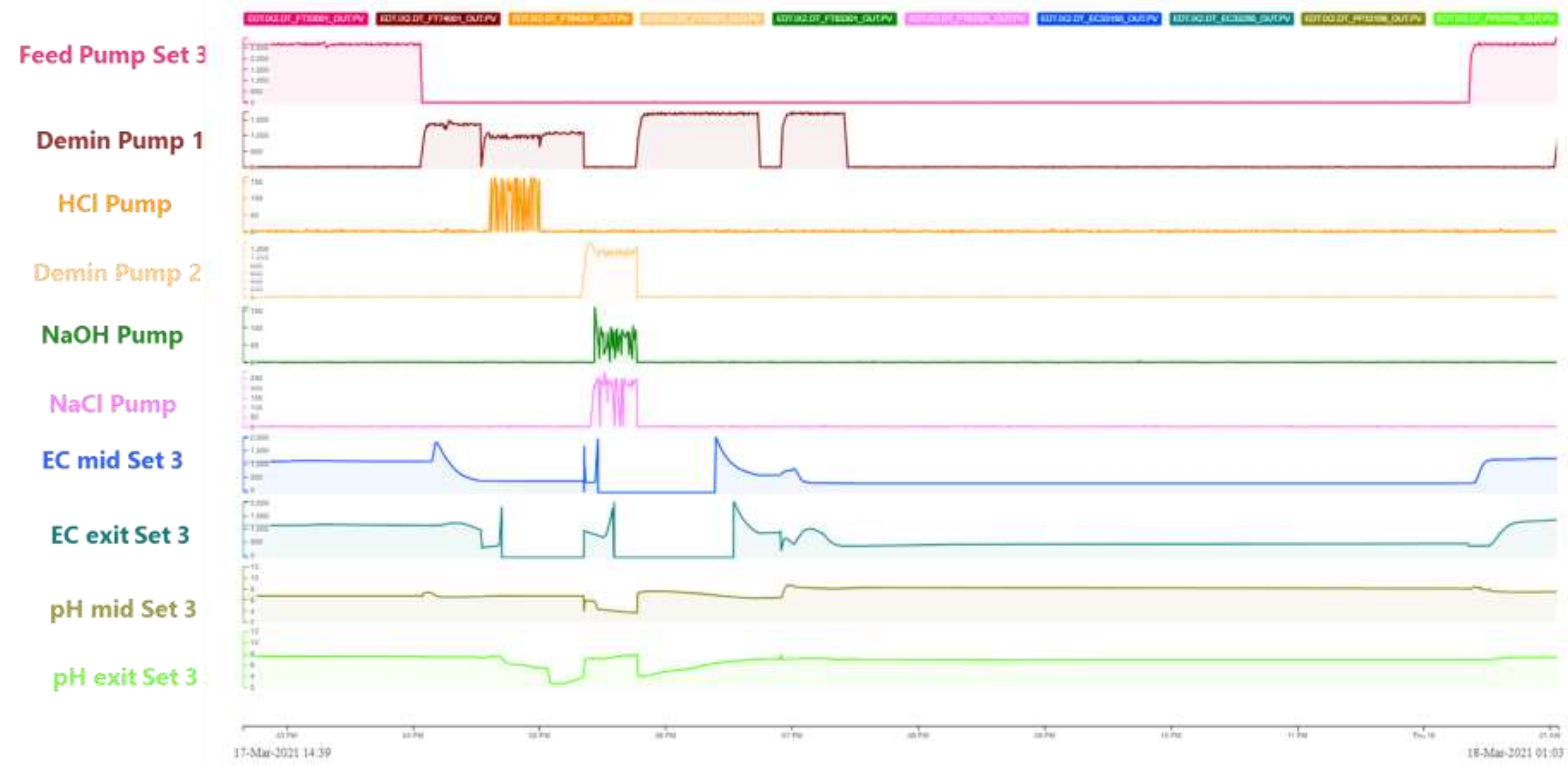


Figure 38: pH patterns during regeneration in Run 3

One hypothesis was that scaling on the resins surface could have been formed, since the displaced water from the WAC columns that passed through the SBA columns contained initially Ca^{2+} and Mg^{2+} ions (above point 1), which could precipitate with CO_3^{2-}, SO_4^{2-} and PO_4^{2-} ions from the SBA resins. Therefore, the scaling on the resin beads could have hindered the SBA resin's OC. To verify this hypothesis by the end of the research period (all 7 runs of **Fout! Verwijzingsbron niet gevonden.**), SCAV4 resin samples were send for analysis to DOW. The results of the resin's analyses can be seen in Annex C) SCAV4 RESIN ANALYSESAnnex C) SCAV4 RESIN ANALYSES. Based on which no scaling was found on the resin's beads, but since the resins are pre-treated before analysis, it could be that the precipitate was dissolved and therefore did not impact the result of the resin analysis.

Another hypothesis was that the low pH during regeneration had a negative effect on the regeneration efficiency but this is very unlikely since hydrochloric acid (HCl) is used in other scavenger systems as the regeneration chemical.

The combined regeneration was then stopped and a couple of double regenerations took place in order to retrieve the lost OC. The OC achieved were higher but not as high as before the combined dosing run as it can be seen in the magenta box of **Fout! Verwijzingsbron niet gevonden.**. Simultaneously, the feed water was changed back to the mixed stream.

Then, some intense regenerations of only the SBA columns with HCl (7.5 times more equivalents than that during the 60 gr NaCl dosing) took place in sets 2 and 3, but not in set 1. From the OCs achieved on those batched (blue box of **Fout! Verwijzingsbron niet gevonden.**) can be seen that not only the OC of sets 2 and 3 (regenerated with intense HCl) were higher but also those achieved with set 1. This is a "mistake" of the control system of the pilot that wrongly though for example that set 2 was exhausted because it was the longest running set while set 1 was really the exhausted one. A couple of batches after the intense regenerations with HCl a new equilibrium was met in resulting in an average OC achieved during Run 4 at 0.43 eq/L_R (having set 1 OC always on the lower side as expected since it was not regenerated intensely). The before mentioned OC is 12.5% lower compared to Run 2, even though in both runs the same regeneration settings and feed water were used. Thus, a part of the OC was permanently lost and it was considered that persistent scaling created during Run 3 to be potentially the reason behind it. As mentioned already before, no persistent scaling was noted on the resin beads and therefore the permanently loss of OC cannot be explained in this way.

From runs 3 and 4, it was concluded that there are still a lot of uncertainties for the application of a combined NaOH and NaCl dosing. The outcomes from the combined dosing test were that (i) indeed less water and time were required for regeneration (benefits points 1 and 2, but (ii) the OC was lowered by 42.5%, thus benefit point 3 was opposite than expected and (iii) the pH during SBA regeneration was lower, thus not higher as expected to be beneficial for TOC removal. Finally, it was noted that even after stopping the combined dosing the OC was not able to be fully restored.

A possible option to avoid the scaling hypothesis and thus OC loss would be to further displace the WAC columns after the HCl dosing. That would entail a higher consumption of water for the HCl displacement (the extra time required could be avoided with higher displacement flow). This option should be further researched, since it is not certain that the same OC with that of separate dosing can be achieved. However, a question someone could ask is "Is it worth it to further research the combined dosing, since in that case the only benefit of it would be the lower time requirements for the regeneration?". More options to be researched in order to have successful combined dosing will be discussed in sub-chapter 4.3.3.

Run 5: Brine Re-use with 60 gr NaCl/L_r & till P in product equal to P in feed/2 & extra Na dosing issue & Run 6: recap run – no brine re-use & till P in product equal to P in feed/2

Once a new equilibrium in the production was reached during Run 4 and the OC was partially restored, the option to use the RO concentrate for the IX regeneration was tested in Run 5 (brine re-use). Specifically, the RO concentrate was used for the following regeneration steps; (i) backwash, (ii) HCl dosing, (iii) NaOH dosing, (iv) NaCl dosing and (v) displacement. Demin water was used only for last regeneration step; the prewash. During Run 5, a new rule was applied to stop the production. This was that the production of the longest running set was stopped at the point where HPO_4^{2-}-P in product was equal half the HPO_4^{2-}-P in feed (≈ 0.3 mg/L). This new rule was used in order to avoid the problem with the over exhaustion of the SBA resins and the subsequent SO_4^{2-} leakage in product water that was noted in previous runs.

The brine re-use for the regeneration operated smoothly for about 7 runs per set (21 in total), resulting on an average OC of 0.427 eq/Lr, which almost the same with the OC achieved with the same chemical dosing for the regeneration but without brine re-use (merely 0.71% lower).

This run was cut short because of a human mistake. Specifically, on 22/04/21 the concentration of the NaOH IBC that were used for the regeneration of the WAC was changed from 25 to 50%, but the settings in the software of IX2 pilot were not changed accordingly. As a results, Na^+ ions dosing was double during WAC regeneration. Thereafter, the OC achieved were lower by 36% (at 0.274 eq/Lr during Run 6). In an effort to find difference that might have caused this loss of OC of the SBA resins due to the extra Na^+ dosing for WAC regeneration it was found that pH before the SBA during the productions of Run 6 was higher compared to Run 5. Specifically, the pH during productions of Run 5 would start from 7.7~7.5 and by the end of production would be around 6.8. In contrast, during Run 6 the pH would start from 9.3 and by the end of production would be around 8.5. The pH patterns during Runs 5 and 6 can be seen in Figure . A valuable conclusion for the full-scale design was that the Na^+ dosing during WAC regeneration should be adjusted in order to ensure that the pH after the WAC and below the SBA columns would be with a range of 8 to 6.5. If an even lower pH could be beneficial was not researched.

Simultaneously, lack of feed water (pilot's operation stopped) and "confusion" on the control program of the productions led again to an over exhaustion of the SBA columns and a leakage of SO_4^{2-} in the product water. For the brine re-use runs, the extra SO_4^{2-} in the product water is an issue that requires the temporarily termination of the brine re-use. Because, even low SO_4^- concentrations in the IX product/ RO feed, would be concentrated by 6.6 times by the ROs (80-85% recovery). The concentrated SO_4^{2-} would return with the regeneration flow to the SBA columns resulting in lower regeneration efficiencies. For this reason, in Run 6 the brine re-use was stopped. The SO_4^{2-} concentrations of the product water as well as the RO concentrate was measured with grab samples. When SO_4^{2-} in both streams was below detection limit, the brine re-use was possible to be re-started. A valuable outcome for the full-scale is to be designed in a way that provides an alternative option of source water for the regeneration in case SO_4^{2-} leaks unintentionally to the IX product and thus to the RO concentrate. And secondly to measure the SO_4^{2-} concentration in the RO concentrate online. Grab samples do not provide enough certainty.

Run 7: Brine Re-use with 60 gr NaCl/Lr & till P in product equal to P in feed/2

Since Run 5 was sort, another run took place to evaluate the performance of the IX2 pilot with re-use of RO concentrate for its regeneration (Run 7). This run was successful with 11 batched per set. The average OC achieved was 0.419 eq/Lr, which was only 2.7% lower than the OC achieved in Run 4 (same regeneration settings – no brine re-use).

Based on product water samples collected from both Run 5 and 7 (brine re-use runs), it was noted that the product water quality during brine re-use was at the same levels with the product water quality during Run 4 (same regeneration settings – no brine re-use). The SO_4^{2-} concentration in product samples was below detection limit. The HPO_4^{2-}-P removal in the runs with brine re-use (Run 5 and 7) was higher than that of the runs without brine – reuse (Run 4). However, this happened due to the new rule to control production (stop production at HPO_4^{2-}-P in product ≈ HPO_4^{2-}-P in feed/ 2) used in Runs 5 and 6 and not to due to the brine re-use. NO_3^- removal was lower in both brine re-use runs (7-9%) compared to Run 4 (14.4%). The RO concentrate that is used for regeneration contains NO_3^- ions. When this water is used for the NaCl regeneration of the SBA resins and the displacement of it, it is expected that NO_3^- will contain a bigger part in the regenerated resin bed compared to a resin bed that was regenerated with demineralized water. As a result, the following production will have smaller capacity for the removal of NO_3^-. Higher NO_3^- concentration in the product water of IX is acceptable as it has been discussed in sub-chapter 3.3.1.

Figure 39: pH during productions of Run 5 and 6 with SCAV4

The TOC concentration in different points of production (from different batches) for the runs without and with brine re-use can be seen in the top graph of Figure . Either with or without brine re-use the TOC in product samples is relatively similar. In some samples from the runs without brine re-use the TOC concentration was higher than the rest. When the TOC in product is presented over the TOC in feed, the differences between the points are smaller (bottom graph of Figure). Moreover, for the two points inside the ellipse, the higher TOC is related to resin's over-exhaustion in the specific batches.

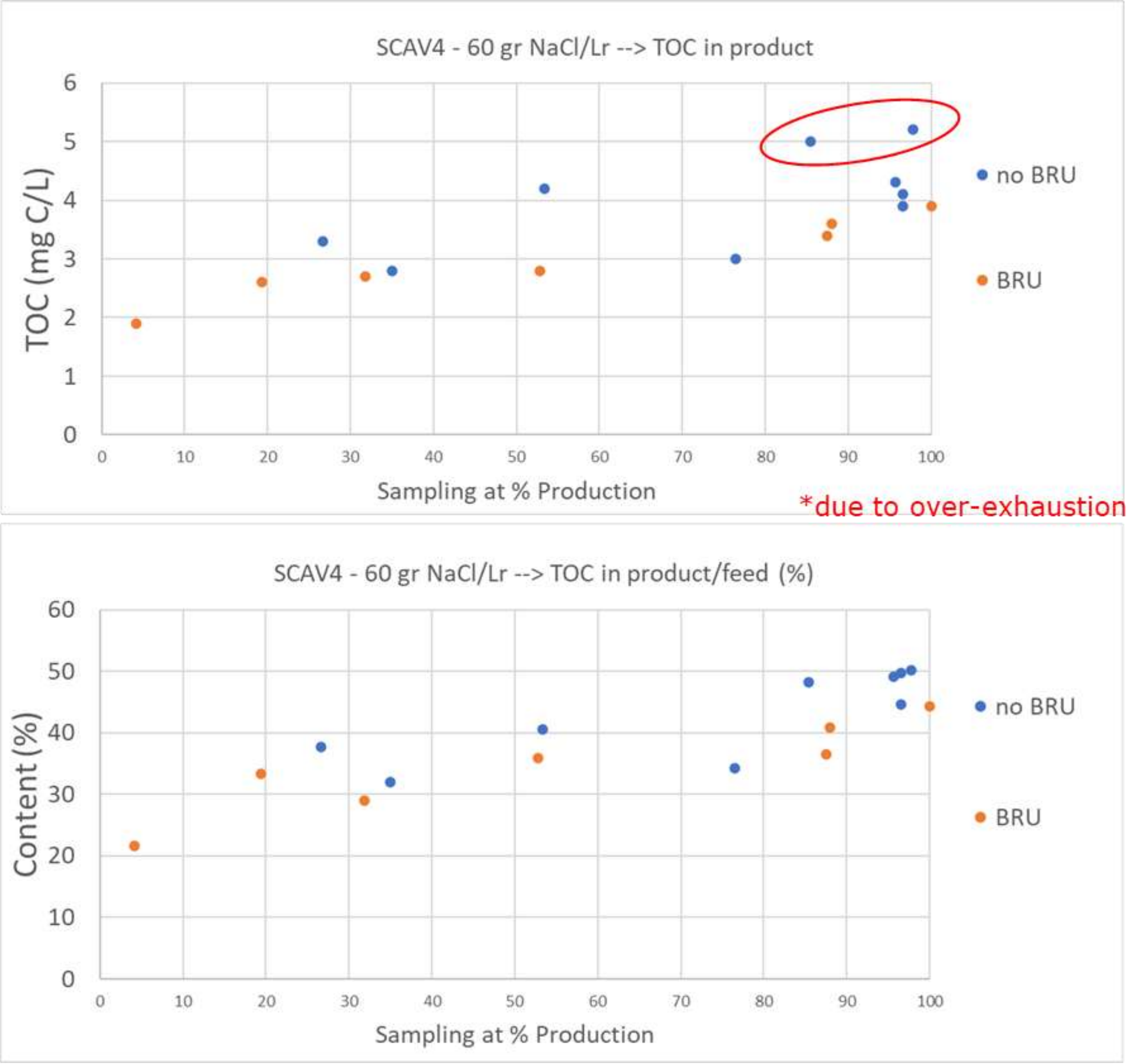


Figure 40: TOC concentration in product samples at different point of production in IX2 with SCAV4 (top). TOC in product over TOC in feed IX2 at different point of production in IX2 with SCAV4 (bottom).

The anions composition in the RO concentrate used for the regeneration can be seen in Table 35. From the anion present in the RO concentrate, Cl^- and HCO_3^- have the bigger contributions at 71.9% and 25.6%, respectively. Then, NO_3^- contributions is only 2.2%. While, HPO_4^{2-}-P and SO_4^{2-} are really low in content. Moreover, in Table 36 the increase of the NaCl dosing because of brine re-use can be seen based on the RO concentrate water quality. The contribution of brine re-use ranges from 0.8 to 2.4% extra NaCl. All in all, the water quality of the RO concentrate explains why brine re-use is possible for the regeneration of the IX unit without significant losses in OC. In contrast a small increase would be expected, but it was not noted in the runs with the SCAV4.

Table 35: RO concentrate used in regeneration anion composition

	Average values
total anion in brine	42.5 meq/L
Cl^- content	71.9 %
HCO_3^- content	25.6 %
NO_3^- content	2.2 %
HPO_4^{2-}-P content	0.08 %
$SO4^{2-}$ content	0.2 %

Table 36: NaCl dosing with and without brine re-use in SCAV4 (Runs 4, 5 and 7)

	NaCl dosing without brine re-use (g/L_R)	**NaCl dosing with brine re-use (g/L_R)**	**Increase (%)**
Min	60	60.5	0.8
Average	60	60.9	1.4
Max	60	61.4	2.4

The main benefit of the brine re-use for the IX regeneration is the higher overall recovery due to the use of the RO concentrate instead of the product water (RO permeate). The water consumption for the regeneration with and without BRU and the subsequent recoveries can be seen in Table 37. The water recovery of IX2 pilot was increased from 92 to 98.5% due to the brine re-use.

Table 37: Recovery of IX2 pilot with and without brine reuse with SCAV4

		Run 4: NO brine re-use	**Runs 5&7: brine re-use**	
	OC (eq/Lr)	0.43	0.42	
	Throughput (L)	65360	63840	
		Required water (L)	Required water (L)	With brine
1	Backwash	678.5	678.5	Yes
2	HCl dosing	542.5	542.5	Yes
3	Displacement	325.5	325.5	Yes
4	NaOH dosing	700	700	Yes
5	NaCl dosing	420	420	Yes
6	Displacement	1700	1700	Yes
7	Rust	-	-	Yes
8	Prewash	850	850	No
	Required demin water (RO permeate)	5216.5	850	
	Recovery (%)	**92**	**98.5**	

Another optimization of the regeneration that took place during Run 7 was the dosing of about half the equivalent of NaOH compared to the dosed HCl equivalents. A conclusion produced based on Runs 5 and 6 (and mentioned already before) was that the pH after the WAC resin and before the SBA resin should be below 8.5. It was considered that reducing the NaOH dosing for the regeneration of the WAC resin to about half the dosing of the HCl, would result in having the WAC resin bed partially regenerated in Na^+ form and partially in H^+ form. Therefore, in the following production the pH after the WAC resin would be lowered since divalent cations would replace Na^+ as well as H^+ ions. Moreover, the HCO_3^- present in the feed water can react with released H^+ ions and result in limited pH changes. To check this point the max total hardness in feed water samples (6 meq/L) was compared to the average HCO_3^- concentration (3.6 meq/L). HCO_3^- cannot uptake 40% of H^+ ions that will be released if all total hardness is removed by the WAC resin. Thus, the dosing of Na^+ was reduced to 40% of the H^+ dosing.

The reduced NaOH dosing test started on 10/05/21 (half way through Run 7). Thereafter, the pH after the WAC column and before the SBA column ranged from 7.5 to 6.5 (compared to 7.7-6.8 before the lower NaOH dosing). There was no negative effect on the OC of the SBA resin. Subsequently, reducing the NaOH dosing to 40% of the HCl dosing, which is related to a 50% reduction in the NaOH dosing, was considered a beneficial option from a perspective of the SBA resins performance. A negative effect on the WAC resin OC is not expected either but it could not be tested in these experiments with IX2 since the WAC resin columns was not exhausted at the time that SBA resin was exhausted. To ensure that the lower NaOH dosing has no negative effect on the WAC resin OC further research should be performed operating only the WAC resin column in IX2.

The chemical consumptions per volume of water produced during Run 4 and Run 7 before and after the lower NaOH dosing for the IX2 pilot is given in Table 38. The chemical consumption during brine re-use is increased by 5.6% in case of NaCl.

Table 38: Chemical consumptions per volume of water produced in case of SCAV4 runs

Chemical dosing per volume of produced water	Run 4	Run 7/ (Run 7 with 50% lower NaOH dosing)
HCl dosing (g/m^3)	266	281
NaOH dosing (g/m^3)	248	262/ (129)
NaCl dosing (g/m^3)	350	370

3.3.4 Results from IX2 research with IRA458

Four runs took place in total with IRA458 used as the SBA resin in IX2 pilot; two with brine re-use and two without. In Table 39 a brief description and the main results of all runs are summarized. The OC calculated for each batch performed in Runs 1 to 4 are given in Figure 41. In this figure the average values from each run and the source of the feed water is shown. The product water quality (significant parameters) and the subsequent removals for Runs 1 to 4 are given in Table 40.

In all 4 runs performed with IRA458 the NaCl dosing used for the regeneration was stable at 80 gr/Lr. Even though it was found that a NaCl dosing of 60 g/L_R was possible for SCAV4 with only 2% lower OC. It was decided to test the regeneration of IRA458 with 60 g/L_R initially with IX1 pilot in parallel to the IX2 experiments. The results of these experiments will be also presented in subchapter 3.3.5.

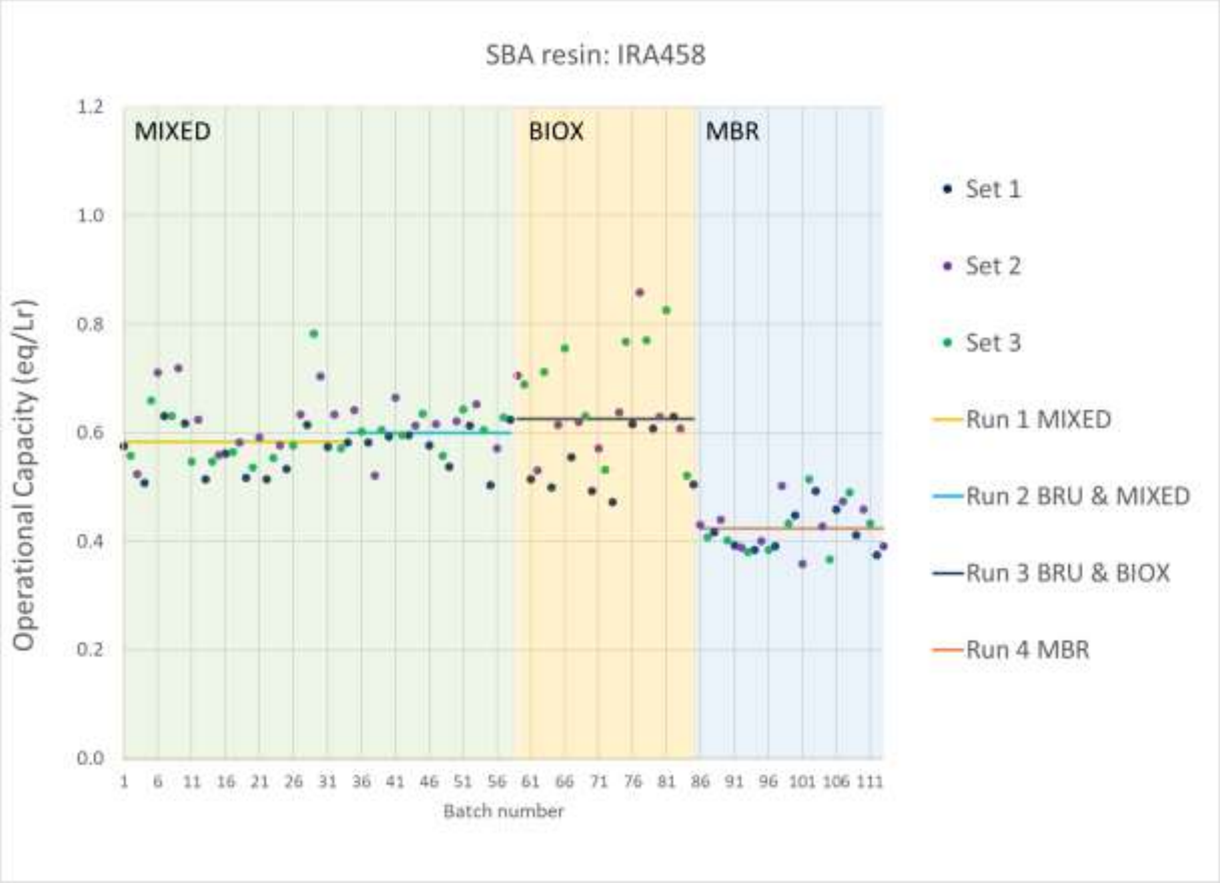


Figure 41: OC achieved in different batches in Runs 1 to 4 with IRA458 in IX2

Table 39: SCAV4 Runs with IX2 - Summary

Run	Dates	Details	Main Result
Run 1: 80 gr NaCl/Lr & till P in product equal to P in feed/2 Feed: Mixed	20/05/21 to 09/06/21	(1) Feed: 100% mixed stream 50/50 BIOX&MBR (2) WAC regeneration: 140% HCl and 60%NaOH over passed equivalents (3) SBA regeneration with 80 g NaCl/L_R (4) Rule: HPO_4^{2-}-P in product ≈ HPO_4^{2-}-P in feed/2 ≈ 0.3 mg/L	**OC = 0.584** eq/Lr based on 100% removal of SO_4^{2-}, 75% removal HPO_4^{2-} and 8% removal NO_3^{2-}
Run 2: Brine Re-use with 80 gr NaCl/Lr & till P in product equal to P in feed/2 Feed: Mixed	10/06/21 to 25/06/21	(1) Feed: 100% mixed stream 50/50 BIOX&MBR (2) WAC regeneration: 150% HCl and 65%NaOH over passed equivalents (3) SBA regeneration with 80 g NaCl/L_r (4) Rule: HPO_4^{2-}-P in product ≈ HPO_4^{2-}-P in feed/2 ≈ 0.3 mg/L (5) All regeneration steps expect of prewash with RO concentrate	**OC = 0.600** eq/Lr based on 100% removal of SO_4^{2-}, 85% removal HPO_4^{2-} and 0% removal NO_3^{2-}
Run 3: Brine Re-use with 80 gr NaCl/Lr & till P in product equal to P in feed Feed: BIOX	26/06/2021 to 18/07/2021	(1) Feed: 100% BIOX (2) WAC regeneration: 180% HCl and 75%NaOH over passed equivalents (3) SBA regeneration with 80 g NaCl/L_r (4) Rule: HPO_4^{2-}-P in product ≈ HPO_4^{2-}-P in feed ≈ 0.3 mg/L (5) All regeneration steps expect of prewash with RO concentrate	**OC = 0.625** eq/Lr based on 100% removal of SO_4^{2-}, 85% removal HPO_4^{2-} and 0% removal NO_3^{2-}
Run 4: 80 gr NaCl/Lr & till P in product equal to P in feed/3 Feed: MBR	20/07/21 to 05/08/21	(1) Feed: 100% MBR (2) WAC regeneration: 160% HCl and 60%NaOH over passed equivalents (3) SBA regeneration with 80 g NaCl/L_r (4) Rule: HPO_4^{2-}-P in product ≈ HPO_4^{2-}-P in feed/3 ≈ 0.3 mg/L	**OC = 0.423** eq/Lr based on 100% removal of SO_4^{2-}, 80% removal HPO_4^{2-} and 8.5% removal NO_3^{2-}

Table 40: Product water quality and removals for Run 1 to 3 with IRA458 in IX2

		Run 1		Run 2		Run 3		Run 4	
Parameter	**Unit**	**Product (mg/L)**	**Removal (%)**	**Product (mg/L)**	**Removal (%)**	**Removal (%)**	**Product (mg/L)**	**Removal (%)**	**Removal (%)**
TOC	mg/L C	3	65	3	65	3	60	3	60
SO_4^{2-}	mg/L	<5	98	<5	98	<5	98	<5	98
NO_3^-	mg/L	18	8	26	0	8.5	0	34	8.5
HPO_4^{2-}-P	mg/L P	0.1	75	0.1	85	0.1	65	0.2	80
Ca^{2+}	mg/L	<0.2	99	<0.2	99	<0.2	99	<0.2	99
Mg^{2+}	mg/L	<0.1	99	<0.1	99	<0.1	99	<0.1	99

Run 1: 80 gr NaCl/L_r & till P in product equal to P in feed/2 & Feed: Mixed

In Run 1, the rule to stop the production and send the longest running set (of the 2 or potential 3 in production) for regeneration was set at the point where the HPO_4^{2-}-P concentration in product was equal to half the HPO_4^{2-}-P concentration in the feed water (≈ 0.3 mg P /L). It must be noted that in this run no over exhaustion of the SBA resin was noted, since the sets were sent to regeneration at correct time following the rule mentioned above.

The feed water throughout Run 2 was the mixed stream 50/50 MBR & BIOX. The average OC achieved was 0.584 eq/L_R based on full removal of SO_4^{2-} , 75% removal of HPO_4^{2-} and 8% removal of NO_3^- feed equivalents.

Comparing Run 1 with IRA458 and Run 1 with SCAV4, it can be seen that IRA458 results in 16% higher OC with the same NaCl dosing for the regeneration of the SBA resins. One difference in operation between the two runs was the rule to stop production. Specifically, in Run 1 with SCAV4 no HPO_4^{2-} was allowed in product and the production was stopped at an earlier point, while in Run 1 with IRA458 HPO_4^{2-} in product would reach 0.3 mg/L and then the production was stopped. If no HPO_4^{2-} was allowed in Run 1 with IRA458 a 6% reduction in the OC is expected (based on the short breakthrough curve of HPO_4^{2-}). Either in this case the OC that can be achieved with IRA458 would still be by 10% bigger than that of SCAV4.

The significant difference in the OCs between IRA458 and SCAV4 was verified with more experiments in IX1 pilot (Figure). Specifically, the same regeneration settings were used for both resins at 80 gr NaCl/Lr and both resins were stopped and send for regeneration at a point where HPO_4^{2-}-P concentration in product was equal to half the HPO_4^{2-}-P concentration in the feed water (about 0.3 mg P /L). Later on, it was found that issues with the NaCl dosing pumps resulted in higher dosing to SCAV4 (about 90g NaCl/L_R) compared to IRA458 (about 80g NaCl/L_R). No matter the OC achieved with IRA458 were almost double than those achieved with SCAV4. Nonetheless, the high difference in OC between the two resins can be trusted.

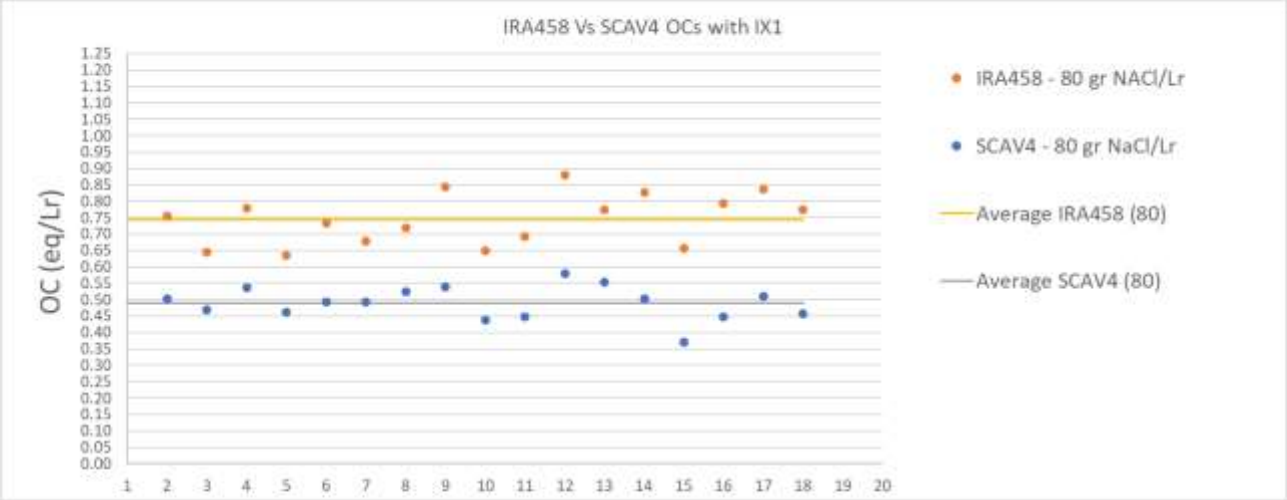


Figure 42: IRA458 and SCAV4 at 80 gr NaCl/Lr regeneration with IX1

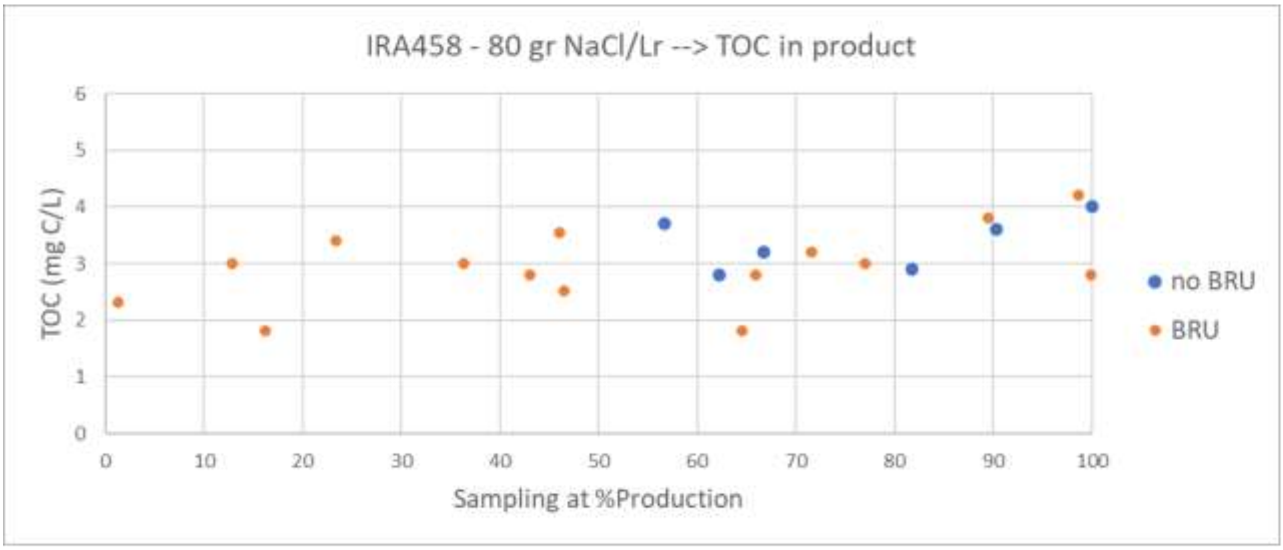
Run 2: Brine Re-use with 80 gr NaCl/Lr & till P in product equal to P in feed/2 & Feed: Mixed

In Run 2 the same regeneration settings (80 gr NaCl/Lr), the same rule for the production (at 0.3 mg P/L) and the same feed water (mixed stream 50/50 BIOX&MBR) with Run 1. The only difference was the use of RO concentrate for the regeneration of the IX2 resins (brine re-use). Specifically, the RO concentrate was used for the following regeneration steps; (i) backwash, (ii) HCl dosing, (iii) NaOH dosing, (iv) NaCl dosing and (v) displacement. Demin water was used only for last regeneration step; the prewash. The average OC achieved was 0.600 eq/L_R based on full removal of SO_4^{2-} and 85% removal of HPO_4^{2-} feed equivalents.

Run 3: Brine Re-use with 80 gr NaCl/L_r & till P in product equal to P in feed & Feed: BIOX

In Run 3 brine re-use was continued with same settings for production and regeneration with Run 2. The feed water though in Run 3 was only BIOX, which resulted in higher OCs with an average of 0.625 eq/Lr based on 100% removal of SO_4^{2-} and HPO_4^{2-} feed equivalents.

Based on product water samples collected from both Run 2 and 3 (brine re-use runs) and the online NO_3^- and HPO_4^{2-} analyzers on the IX2 product steam, it was noted that the product water quality during brine re-use was at the same levels with the product water quality during Run 1 (same regeneration settings – no brine re-use). The SO_4^{2-} and HPO_4^{2-}-P concentration in the product remained at the same level. However, no NO_3^- removal was noted in the brine re-use runs, which is an expected outcome since the RO concentrate that is used for regeneration contains NO_3^- ions and thus after regeneration a bigger part in the regenerated resin bed will contain NO_3^- compared to a resin bed that was regenerated with demineralized water. The TOC concentration in different points of production (from different batches) for the runs without and with brine re-use can be seen in the top graph of Figure . Either with or without brine re-use the TOC in product samples is relatively similar.



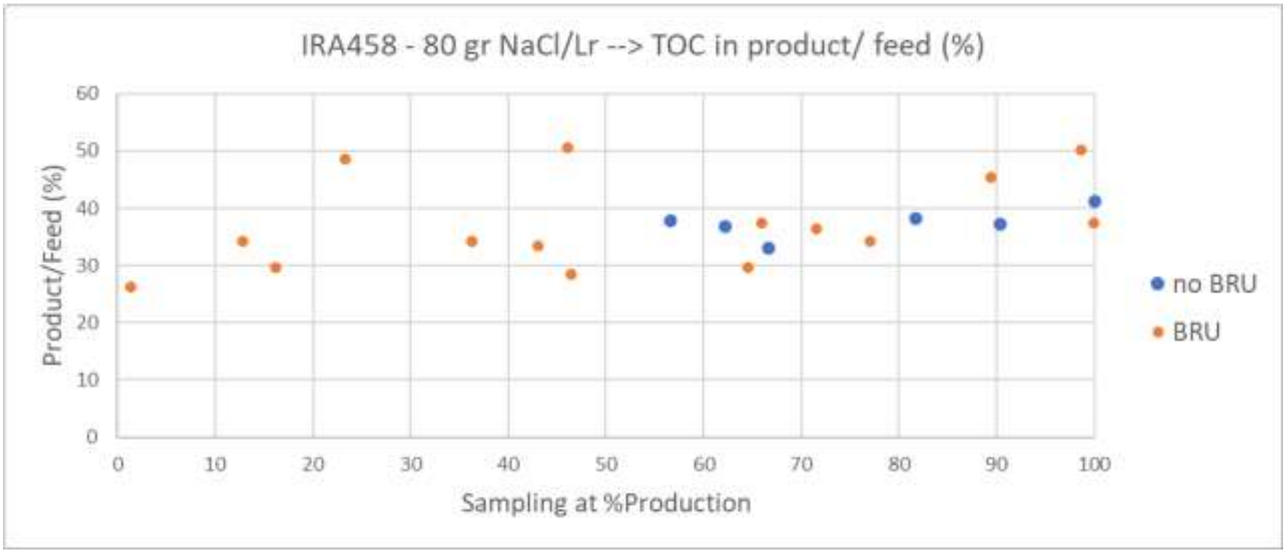


Figure 43: TOC concentration in product samples at different point of production in IX2 with IRA458 (top). TOC in product over TOC in feed IX2 at different point of production in IX2 with IRA458 (bottom).

Comparing the OCs achieved in Run 1, 2 and 3, it is noted that:

1) Run 2 (brine re-use) average OC is 2.7% higher than that of Run 1 (same regeneration settings & same feed water - no brine re-use). This result is in accordance to the increase in the NaCl dosing due to Cl^- present in the RO concentrate (Table 41). The anions composition in the RO concentrate used for the regeneration was given in the previous sub-chapter in Table 35. The water quality of the RO concentrate explains why brine re-use is possible for the regeneration of the IX unit with a small increase on the OC due to more Cl^-, HCO_3^- and NO_3^- ions available for the regeneration.
2) Run 3 (brine re-use with only BIOX) average OC is 4% higher than that of Run 2 (brine re-use with mixed & same regeneration settings). It is noted that the use of only BIOX as feed water in the brackish water line results in higher OCs and the same effect was noted in Run 2 with SCAV4. The above outcome can be explained if the anions content in the mixed stream are compared to those in BIOX (Table 42). BIOX contains 37% lower amount of competitive equivalents (Cl^-, HCO_3^-, and NO_3^-) compared to the mixed stream (due to MBR contribution). As a results, when the mixed stream is used for the production, SO_4^{2-} and HPO_4^{2-} have more competition during ion exchange and that results in an earlier breakthrough of HPO_4^{2-} and therefore in lower OCs.
3) Run 3 (brine re-use with only BIOX) average OC is 6.5 % higher than that of Run 1 (same regeneration settings - no brine re-use with mixed stream). This increase is partly due to the brine-reuse and partially due to the use of BIOX as the feed of the brackish water line.

Table 41: NaCl dosing with and without brine re-use in IRA458 (Runs 1, 2 and 3)

	NaCl dosing without brine re-use (g/L_R)	NaCl dosing with brine re-use (g/L_R)	Increase (%)
Min	80	80.6	0.7
Average	80	81.1	1.4
Max	80	81.9	2.3

Table 42: Mixed Vs Biox anions

Feed source	Mixed	BIOX	BIOX - Mixed	BIOX - Mixed
Unit	**meq/L**	**meq/L**	**Difference (%)**	**Total Difference (%)**
Cl^-	5.57	2.88	↓ 48%	↓ 37%
HCO_3^-	3.43	2.86	↓ 16%	
NO_3^-	0.38	0.1	↓ 73%	
HPO_4^{2-}-P	0.06	0.02	↓ 65%	↑ 13%
SO_4^{2-}	2.00	2.4	↑ 15%	
Targeted anions/total (%)	18.6%	29.3%	-	-

The main benefit of the brine re-use for the IX regeneration is the higher recovery due to the use of the RO concentrate instead of the product water (RO permeate). The water consumption for the regeneration with and without BRU and the subsequent recoveries for Runs 1 and 2 with IRA458 can be seen in Table 43. The water recovery of IX2 pilot was increased from 94 to 99% due to the brine re-use.

Table 43: Recovery of IX2 pilot with and without brine reuse with IRA458

		Run 1: NO brine re-use	**Runs 2: brine re-use**	
	OC (eq/Lr)	0.584	0.600	
	Throughput (L)			
		Required water (L)	Required water (L)	With brine
1	Backwash	678.5	678.5	Yes
2	HCl dosing	542.5	542.5	Yes
3	Displacement	325.5	325.5	Yes
4	NaOH dosing	700	700	Yes
5	NaCl dosing	420	420	Yes
6	Displacement	1700	1700	Yes
7	Rust	-	-	Yes
8	Prewash	850	850	No
	Required demin water (RO permeate)	5216.5	850	
	Recovery (%)	**94**	**99**	

Run 4: 80 gr NaCl/Lr & till P in product equal to P in feed/3 & Feed: MBR

In Run 4 the brine re-use for the regeneration of the IX was stopped, the same regeneration settings were used with the previous runs (80 gr NaCl/Lr) as well as the same rule to stop production (at 0.3 mg P/L). The feed water though in Run 4 was only MBR, which resulted in a decrease of the OCs with an average of 0.423 eq/Lr (27.5% smaller than that of Run 1) based on 100% removal of SO_4^{2-}, 80% removal HPO_4^{2-} and 8.5% removal NO_3^{2-}. Since brine re-use stopped, NO_3^- was again partially removed during production.

The use of MBR as feed water in the brackish water line during this run resulted in lower OCs. The same effect was noted in Run 3 with SCAV4. The above outcome can be explained if the anions content in the mixed stream are compared to those in MBR (Table 44). MBR contains 37% higher amount of competitive equivalents (Cl^-, HCO_3^-, and NO_3^-) compared to the mixed stream (due to BIOX contribution). As a results, when MBR is used for the production, SO_4^{2-} and HPO_4^{2-} have more competition during ion exchange and that results in an earlier breakthrough of HPO_4^{2-} and therefore in lower OCs.

If the MBR run (Run 4) is compared with the Biox run (Run 3), the difference is even more significant at 31% lower operational capacity during Run 4. This decrease can partially attributed to no brine re-use, but mostly to the difference in the anion composition of MBR and Biox as given in Table 45.

Moreover, the fact the drop of the OC from Mixed to MBR is more significant than the rase of the OC from Mixed to Biox can be explained from the ratios between the target anions (SO_4^{2-} and HPO_4^{2-}-P) over the total anions as given in Table 44 and Table 45. The step up from mixed to Biox is bigger than the step down from mixed to MBR, therefore the lower competition in Biox case is less significant than the higher competition in MBR case comparing both to the mixed.

Table 44: Mixed Vs MBR anions

Feed source	**Mixed**	**MBR**	**MBR - Mixed**	**MBR - Mixed**
Unit	**meq/L**	**meq/L**	**Difference (%)**	**Total Difference (%)**
Cl^-	5.57	8.25	↑ 48%	↑ 37%
HCO_3^-	3.43	4	↑ 16%	
NO_3^-	0.38	0.65	↑ 73%	
HPO_4^{2-}-P	0.06	0.1	↑ 65%	↓ 13%
SO_4^{2-}	2.00	1.75	↓ 15%	
Targeted anions/total (%)	18.5%	12.5%	-	**-**

Table 45: MBR Vs BIOX anions

Feed source	MBR	BIOX	MBR - BIOX	MBR - BIOX
Unit	**meq/L**	**meq/L**	**Difference (%)**	**Total Difference (%)**
Cl^-	8.25	2.88	↓ 65%	↓ 54%
HCO_3^-	4	2.86	↓ 28%	
NO_3^-	0.65	0.1	↓ 84%	
HPO_4^{2-}–P	0.1	0.02	↓ 80%	↑ 30%
SO_4^{2-}	1.75	2.4	↑ 37%	
Targeted anions/total (%)	12.5%	29.3%	-	**-**

During all 4 runs with IRA458 the dosing of NaOH was half the equivalents of the HCl dosed equivalents in order to maintain the pH after the WAC column and before the SBA column in low level (≈ 8 to 6). The results per run were:

1) Run 1: 8.5 to 6
2) Run 2: 8.5 to 8.5
3) Run 3: 9 to 7
4) Run 4: 8.56 to 6

The lower dosing again did not seem to have any negative effect on the OC of the SBA and on the removals of Ca^{2+} and Mg^{2+} up to the point that production was stopped. WAC exhaustion was not reached at any batch, since the WAC resin columns are not exhausted at the time that SBA resin columns are exhausted in the way IX2 pilot was used. To ensure that the lower NaOH dosing has no negative effect on the WAC resin OC further research should be performed operating only the WAC resin column in IX2 pilot.

The chemical consumptions per volume of water produced during Runs 1 to 4 of IRA458 in IX2 pilot is given in Table 46.

Table 46: Chemical consumptions per volume of water produced in case of SCAV4 runs

Chemical dosing per volume of produced water	Run 1	Run 2	Run 3	Run 4
HCl dosing (g/m^3)	245	239	229	339
NaOH dosing (g/m^3)	114	111	107	158
NaCl dosing (g/m^3)	342	333	320	473

Finally, in all runs with IRA458 no constant over exhaustion of the SBA resin was noted (only two times in all 4 runs), since the sets were sent to regeneration at correct time following the rule to stop the production and send the longest running set for regeneration at the point where the HPO_4^{2-}-P concentration in product was equal to ≈ 0.3 mg P /L. For Runs 1 and 2, 0.3 mg P/L was about half the HPO_4^{2-}-P concentration in the feed water. For Run 4, it was even less than half and specifically the one third of the feed concentration. Even in Run 3, that 0.3 mg P/L was equal to the feed concentration, no over-exhaustion was noted. This results apart of the production rule that gives some space before the over exhaustion and the SO_4^{2-} leakage can be also attributed to a smooth pattern in regeneration sequence. However, this can be easily disturbed (e.g. by an error in the HPO_4^{2-}-P analysers in the product water that controls production length). Therefore, in the full-scale design (i) organised monitoring of the analysers is required and (ii) an alternative plan in case of leakage of SO_4^{2-} in the product water if the RO concentrate is used for the IX regeneration (brine re-use).

3.3.5 Results from SCAV4 and IRA458 SBA resins experiments with IX1 pilot (research 2021)

In Figure the OCs for both SCAV4 and IRA458 at regeneration levels 80 and 60 gr NaCl/Lr is given. In all batches, the feed water was the mixed stream and the SBA resins were stopped and send for regeneration at a point where HPO_4^{2-}-P concentration in product was equal to half the HPO_4^{2-}-P concentration in the feed water (about 0.3 mg P /L). In the first part of the graph the aimed dosing was 80 gr/Lr (already presented in Figure of the previous chapter). In the second part of the graph the aimed dosing was 60 g/L_R. Later on, it was found that issues with the NaCl dosing pumps resulted in higher dosing towards SCAV4 of about 90 and 70g NaCl/L_R, respectively for the two parts. Another issue with IX1 pilot operation was that before some batches multiple regenerations took place due to problems with the HPO_4^{2-}-P analyser. Specifically, 3 regenerations before batches 9, 36 and 49, 2 regenerations before batches 21 and 30 and 10 regenerations before batch 48.

A big contrast between the OCs achieved in these experiments with IX1 and the experiments with IX2 was noted. Important differences in the operation and regeneration settings were the following:

1) Only the SBA resin columns were used; thus, the water before the SBA resin was not softened, while in 2020 experiments with IX1 and in the experiments with IX2 it was.
2) The pH before the SBA columns was between 6-7.
3) The NaCl dosing with IX1 was 90 and 70 gr/Lr instead of 80 and 60 gr/Lr that it was with IX2.
4) The HPO_4^{2-}-P concentration of the product water from the SBA resins in IX1 was measured separately for one resin column. When the exhaustion set point (0.3 mg P/L) was met the production was stopped. However, in IX2 the product water quality of the mixed stream of 2 or potentially 3 SBA columns was measured and the running longest set was sent for production when the exhaustion set point was met. Thus, the contribution of the about to be exhausted set to the mixed stream was either 1/2 or 1/3, therefore each set was able to stay in production for a longer time.
5) In Run 1 of SCAV4 with IX2 the exhaustion point was at < 0.1 mg P/L in the product water, while in Run 2 the exhaustion point was at 0.6 mg P/L in the product water. If in both cases the exhaustion point of 0.3 mg P/L was used then the OC of Run 1 would be a bit higher and the OC of Run 2 would be a bit lower.

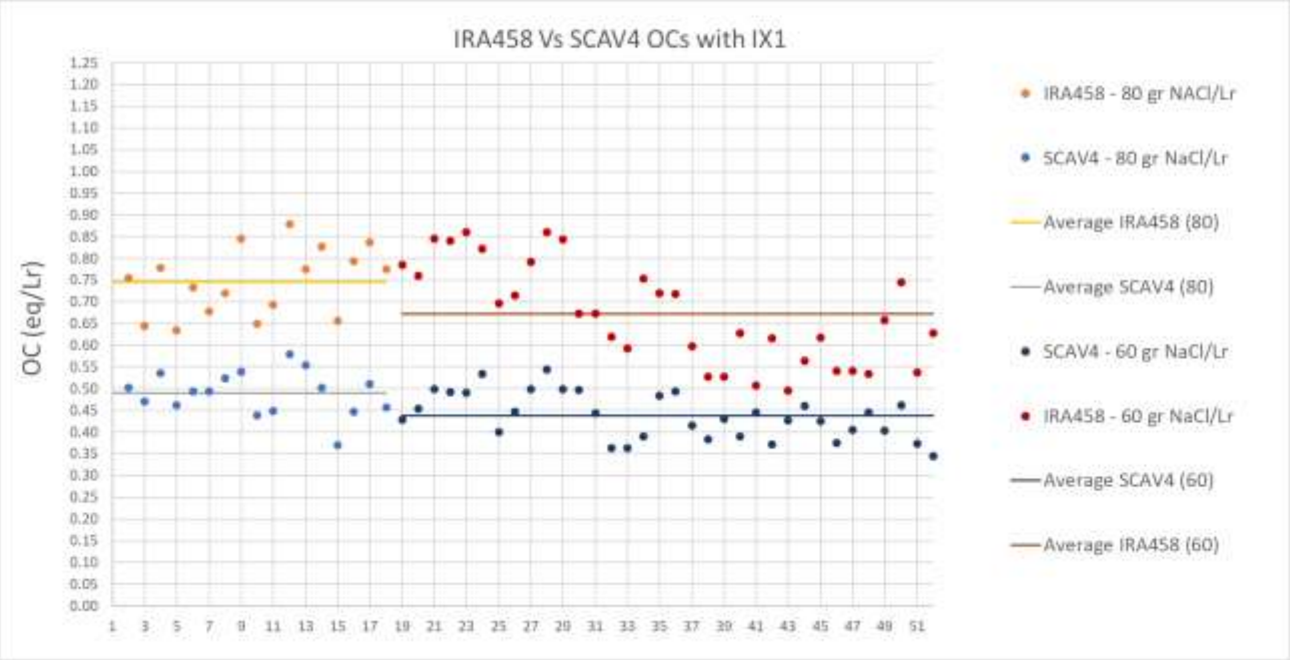


Figure 44: IRA458 and SCAV4 at 80 gr NaCl/Lr and 60 gr NaCl/Lr regeneration level with IX1

In the experiments with IX1 there were so many inaccuracies and uncertainties that is not worthy to compare results between the two pilots. But, some valuable point from the experiments with IX1 pilot (2021 research) were made. These were:

1) In all batches performed IRA458 OC is bigger than the OC of SCAV4 by an average value of 34%, even though, the NaCl dosing towards SCAV4 was in all batches more than that towards IRA458.
2) As mentioned earlier the pH before the SBA columns was between 6-7 (thus lower than in IX2 and IX1 (2020 research) experiments and the OC achieved was higher. Thus, again it is noted that lower pH during production before the SBA is beneficial for the exchange of the ions and the resulting OC.

3) The decrease in the NaCl dosing for SCAV4 from 90 to 70 g/L_R (22%) and for IRA458 from 80 to 60 gr/L_r (25%) has a negative effect to the OCs of both resins but more significant to IRA458. As it can be seen in Figure , for IRA458 after the lower NaCl dosing starts initially the OCs stay at the same level with the run 80 g/L_R (this happens partially due to some batches with multiple regenerations). Then, after a few more runs the OCs drop significantly. But, as mentioned already the values calculated with these experiments cannot be trusted. Thus, the questions that remains is how much lower will the OC due to 60 g NaCl/L_R be and whether or not in comparison to the reduction of chemical use is beneficial. It is necessary to research this option with IX2 pilot before it is considered for the full-scale design.

3.4 Reverse-osmosis

The RO research started on 31st of August 2020 and will run until 31st of December 2021. From August 31st until December 24th 2020, some smaller runs were performed with the pilots to gain some first insights on the performance. Some hardware issues occurred in the first month, but after this start-up period, the pilots were operated in a more constant manner. From 29th of December 2020 until the end of the project a longer run was performed to gain insight in long-term operational trends. An overview of the different runs performed with the RO pilots is given in the table below.

Table 47: Overview runs RO.

Research period	Run	Remarks
31/08/2020 – 29/09/2020	UF-RO's	Hardware issues: • Wrong MTC measurements for RO-Groot and RO-scaleguard due to data watt issues; • Wrong NPD measurement for biofouling guard due to wrong pressure measurement; • Downtime of > 50% due to lack of feedwater
06/10/2020 – 20/11/2020	CW-UF-biofouling guard	
09/10/2020 – 23/11/2020	CW-UF-IX1-biofouling guard	• IX1 not producing continuously. Permeate and Concentrate of RO are recycled back to the feed tank of the RO. • Effects of recirculating are unknown • Phosphate is not removed by IX1 (2mg/L in feed RO)
30/11/2020 – 24/12/2020	CW-UF-IX1-RO-Groot-scaleguard	• IX1 not producing continuously. Permeate and Concentrate of RO-Groot and scaleguard are recycled back to the feed tank of the RO. • Effects of recirculating are unknown • Phosphate is not removed by IX1 (2mg/L in feed RO)
28/12/2020 – 31/08/2021	CW-UF-IX2-RO's	• Higher salt passage in RO-Groot due to leakage; fixed on 22/04/2021 • Bad flow measurements of biofouling guard from 17/06/2021 – 21/06/2021 • Datawatt issues biofouling guard from 04/08/2021 – 12/08/2021 Important changes in settings: • 08/02/2021: Higher P concentration in feed • 01/03/2021: Start brine reuse UF • Different periods of brine reuse IX2: o 13/04/2021 – 26/04/2021 o 30/04/2021 – 18/05/2021 o 13/06/2021 – 19/07/2021 • 17/06/2021: Flux to 18.6 LMH for RO-Groot and RO scaleguard • 15/07/2021: New membrane in RO scaleguard • 30/08/2021: New membrane in RO biofouling guard

The design assumptions for the full-scale design were tested in the pilot set-up. Multiple issues occurred that made a stable operation of the RO pilots with the selected settings challenging. The different issues and findings are discussed in the chapter below.

3.4.1 Fouling issues

The MTC progress for all pilots during the long run is given in Figure 45. A really sharp decrease of MTC can be seen in the first 3 days of operation; being 23%, 25% and 28% for respectively the biofouling guard, RO-Groot and the scale guard. This period is seen as a stabilization period and values are not taken into account. Values after stabilization are 1.44 m/s.Pa for the biofouling guard, 1.64 m/s.Pa for RO-Groot and 1.13 m/s.Pa for the scale guard. These values are seen as beginning values for MTC. According to WAVE the value for RO-Groot resembles a fouling factor of 0.8, which is the wanted yearly average.

A continuous MTC decline is noticed since the beginning of operation. Moreover, it is not possible to bring the MTC back to original values with standard caustic and acid CIP's. The decline is similar in all pilots. After 5 months of operation, the MTC lowered with 37.5% for the biofouling guard, 39.6% for RO-Groot and 34.5% for the scale guard, despite all the CIP's performed. This MTC decrease indicates that some fouling is covering the pores of the membranes and therefore lowering the porosity. The fouling is happening in the same extend on all membranes, from the first element to the last one; this is typical for organic fouling or biofouling. In the latter case, you would also expect spacer pollution which is not the case here.

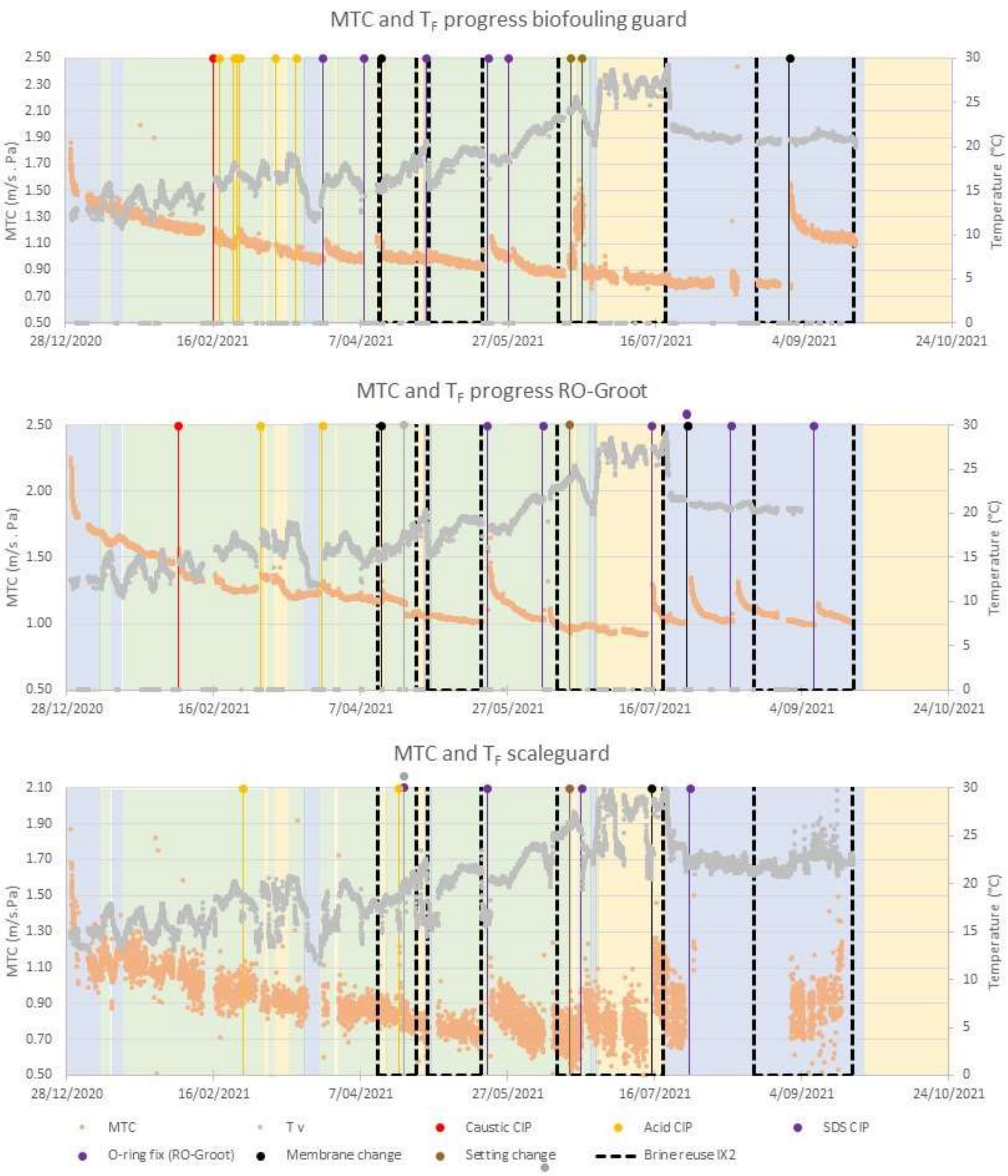


Figure 45: MTC (orange) and feedwater temperature (grey) progress for all pilots during CW-UF-IX2-RO run (blue background = MBR as feedwater source; yellow background = biox as feedwater source; green background = mix as feedwater source).

Different factors can be responsible for this MTC decrease seen in the RO pilots:

i. Type of pre-treatment: an unknown substance can leach out of the argex pellets in the wetland or out of the IX resins and slowly foul the RO membranes.
ii. Type of feedwater: biox contains some unknown substances coming from the chemical activities performed at Dow, while MBR permeate can contain some medicines or other components coming from the domestic wastewater of the city Terneuzen. One of these substances in the feedwater can cause the membranes to foul. Also in the E4Water research the NF pilot did not have a stable MTC while running on biox.

<u>Fouling due to pretreatment steps?</u>

As mentioned before, multiple short runs were performed with the biofouling guard in order to gain some first insights. For every run a new membrane was placed in the pilot. The MTC progress of all short runs was plotted over the runtime of the pilots and compared to the MTC progress of the biofouling guard in the long run. It has to be noted that the membrane in the UF-RO run is a new membrane, but the membrane was preserved for 5 months in a 2% sodium bisulfite solution due to a long shutdown of the pilots after the membrane was placed. Probably because of this fact the sharp decrease in the beginning cannot be seen in this run and MTC values are somewhat different than in the other runs. However, the decline seems to have the same slope in all experiments (Figure 46).

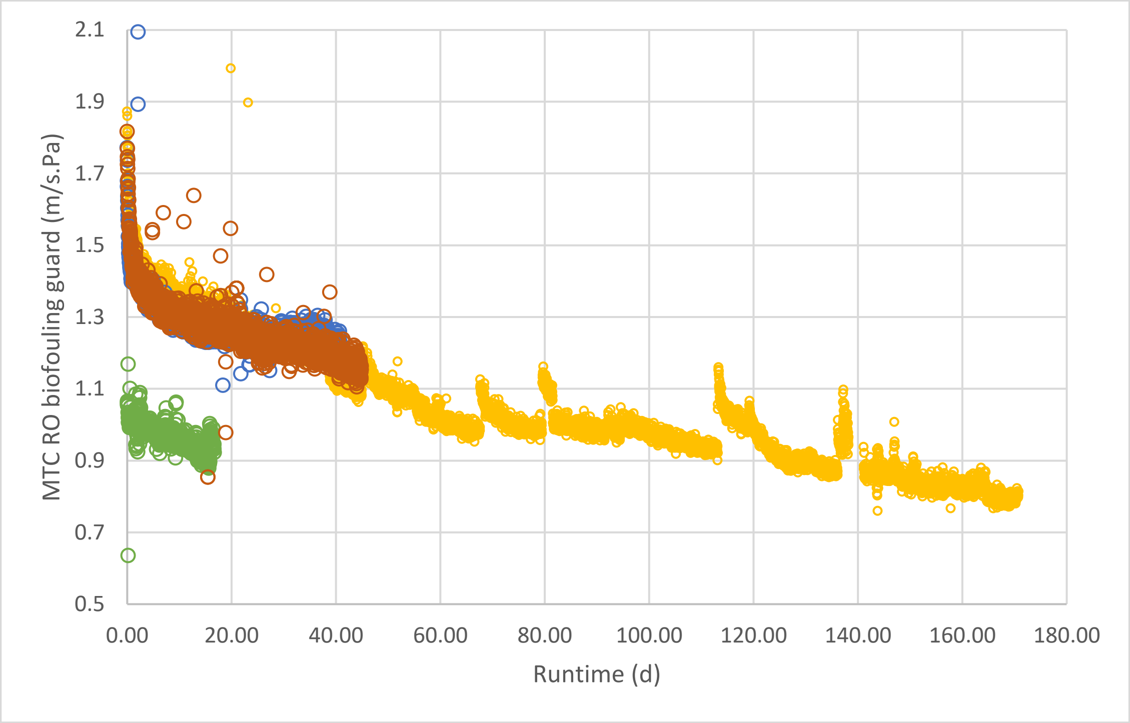


Figure 46: MTC progress of the biofouling guard for all runs. Green = UF-RO; blue = CW-UF-RO; orange = CW-UF-IX1-RO; yellow = CW-UF-IX2-RO

It is clear from the graph that a comparable MTC decrease can be seen in all runs. It can be concluded that the substance causing the fouling on the RO membranes is not removed by either of the pretreatment techniques, not by the wetlands, nor the UF or ion exchange, but is ending up on the RO membranes.

Fouling due to type of feedwater source?

Since MBR permeate is already treated in the EWRO pilot operating at Deco and no MTC decrease is occurring there, it is unlikely that the MBR permeate is responsible for the fouling of the membranes. To check the effect of the different feedwater sources, the MTC decrease of RO-Groot for periods with different feedwater sources is compared. As mentioned before, the steep decrease in the beginning is seen as a stabilization period. When looking at the MTC decrease of RO-Table 48 it is clear that periods with biox or mix as a feed source give a higher MTC decrease per day compared to periods were MBR was the feed source. Switching to MBR after the mixture results in a small increase of MTC. It can be concluded that the MTC is decreasing faster in periods when only biox or when the mix was used as feed source compared to periods where MBR was used as feed source. The component causing the membranes to foul is therefore most likely present in the biox stream.

Table 48: MTC decrease for multiple periods with different feedwater source.

	Period	# days	MTC start	MTC end	**decrease / day**
stabilization	29/12 15:00 – 04/01 15:00	6.00	2.26	1.74	**3.84%**
MBR	4/01 15:00- 09/01 0:00	4.38	1.74	1.68	**0.79%**
mix	9/01 0:00 – 11/01 20:00	2.83	1.68	1.6	**1.68%**
MBR	11/01 20:00 – 16/01 1:00	4.21	1.6	1.64	**-0.59%**
mix	16/01 1:00 – 2/03 4:30	45.15	1.64	1.26	**0.51%**
biox	9/03 16:00 – 16/03 16:00	7.00	1.33	1.2	**1.40%**
mix	17/03 4:00 – 19/03 2:00	1.92	1.24	1.21	**1.26%**
MBR	19/03 2:00 – 23/03 2:00	4.58	1.21	1.23	**-0.36%**
mix	25/03 12:00 – 29/03 7:00	3.79	1.3	1.23	**1.42%**

Multiple membranes were sent for autopsy. The report confirmed a flow decline that cannot be restored with common caustic (NaOH) or acidic (HCl) cleanings. These results conclude the findings in the pilot test. More research was performed in the lab to identify the component on the membranes and results will be explained in a later section.

3.4.2 Biofouling issues

Previous bio growth potential tests showed really low potential of the feedwater for micro-organisms to grow. If fouling and/or bio growth is attaching to the feed spacer of the RO membranes, the NPD rises. NPD progress during the long run is plotted along with the temperature in Figure for all pilots. Same as for the MTC, the first three days of operation is seen as a stabilisation period and these values are left out of consideration. Beginning values of NPD are 0.18bar, 1.74bar and 0.18bar for the biofouling guard, RO-Groot and the scale guard respectively which is in the range of expected values.

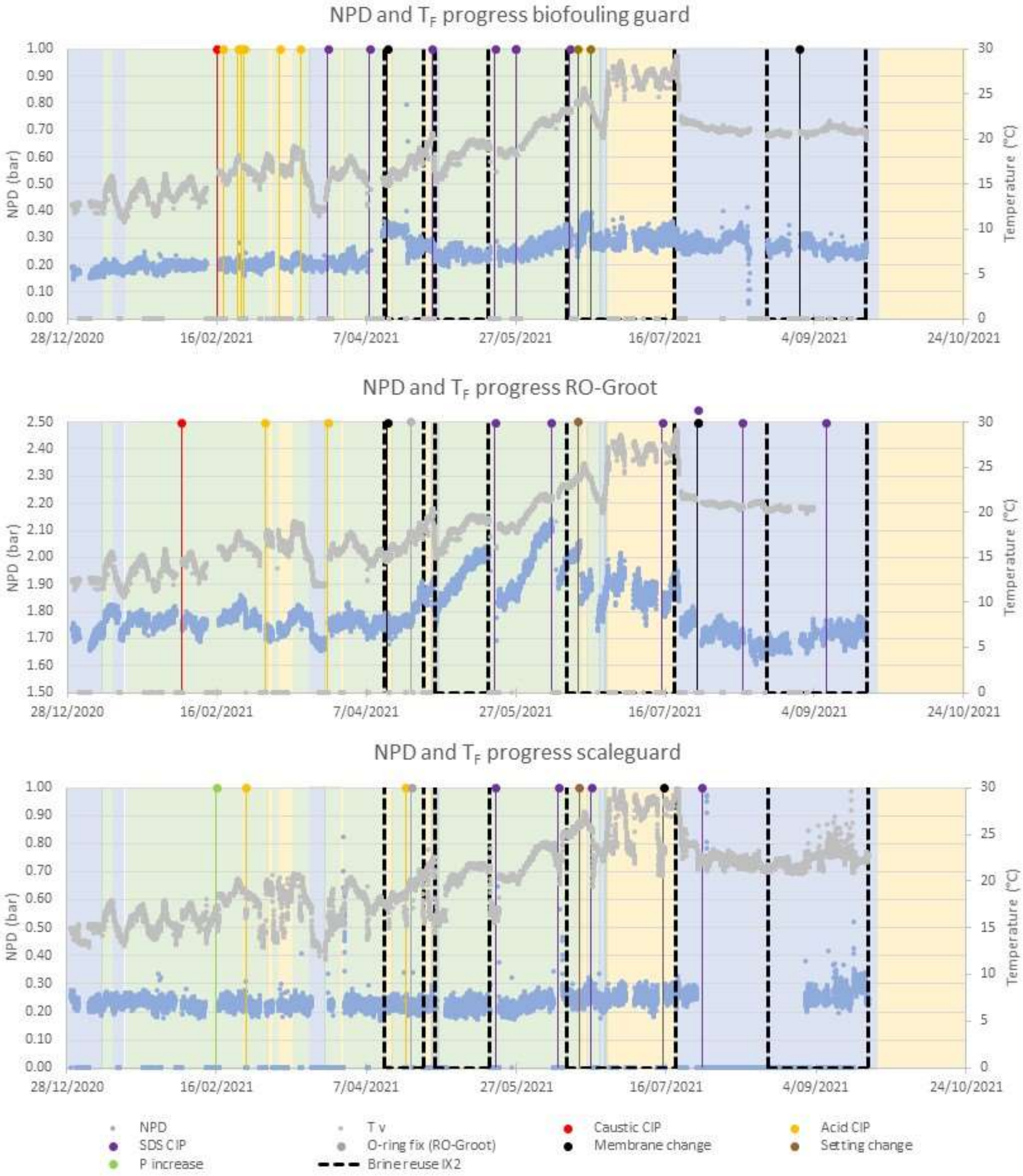


Figure 47: NPD (dark blue) and feedwater temperature (grey) progress for all pilots during CW-UF-IX2-RO run (blue background = MBR as feedwater source; yellow background = biox as feedwater source; green background = mix as feedwater source).

A stable NPD can be seen in the first part of the run. On February 8th it was decided to increase the operational capacity of the ion exchange by increasing the amount of P in the feedwater of the RO's to 0.3 mg/L. This higher amount of P does not lead to extra bio growth, since NPD stays stable after this change. NPD stays stable until mid April. Somewhere between 22/04/2021-30/04/2021, NPD of the biofouling guard and RO-Groot start rising, while the NPD of the scale guard stays more stable throughout the whole experiment. In that period feedwater temperature is also rising from 15°C to 19°C. It is known that in warmer periods biofouling is more likely to occur. Fouling in the spacer is therefore only present in the first elements in warmer periods of the year.

Some tests were performed in parallel with Membrane Fouling Simulators (MFS units). These units are designed to quickly predict fouling issues in the spacer. The MFS tests confirm stable operation until mid April. ΔP over the flow cell accepting IX product stays stable for the first months and starts increasing in April. At the end of the run, a layer of fouling can be visually seen on the spacer of the membrane (Figure 48).

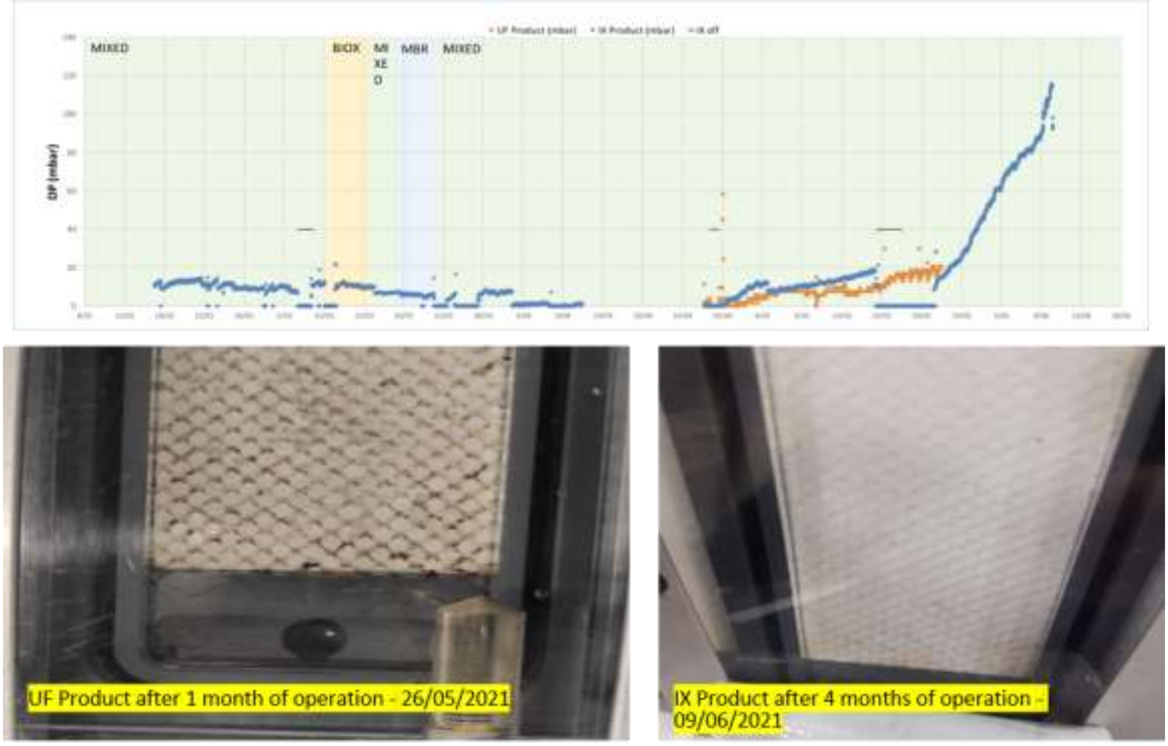


Figure 48: Top = ΔP progress of the MFS unit accepting IX product (blue) and the MFS unit accepting UF permeate (orange) during February to May; Bottom left = picture of the MFS UF membrane at the end of the run; Bottom right = picture of the MFS IX membrane at the end of the run.

After changing the flux to 18.6LMH on the 17th of July, the NPD of RO-Groot is lower than with a flux of 21LMH. Afterwards, the NPD of RO-Groot starts lowering even more at the end of June when the pilots when running on biox, while the NPD of the biofouling guard stays stable at this higher level and is not increasing anymore. During that period also temperature stays stable around 27°C. A bigger decrease can be seen in July when the pilots were running on MBR permeate only, because of the switch to MBR also temperature lowered to 20°C. This temperature decrease probably leads to lower biofouling potential of the feedwater. This is confirmed by the tests performed in parallel with the MFS units. The ΔP progress of the MFS unit accepting IX product and UF permeate is shown in Figure 49. The ΔP increase over the membrane accepting UF permeate is slowing down in the period where MBR is set as feedwater. The ΔP increase over the membrane accepting IX product is 2 times as fast (40mbar increase in 14 days) when biox was the feed source compared to MBR as feed source (20mbar increase in 14days).

Figure 49: ΔP progress of the MFS unit accepting IX product (blue) and the MFS unit accepting UF permeate (orange) during June to August; two membranes were placed in MFS IX (15/06/21-15/07/2021 & 23/07/2021-19/08/2021), while only 1 membrane was placed in the MFS UF (21/06/2021-19/08/2021)

It is not clear why the NPD starts rising in April and is lowering in June. Multiple events or factors can add to this NPD rise/decline:

i. Warmer temperatures: it is known that biofouling is more likely to occur in warmer periods (spring and summer). The highest NPD rise can also be seen in the period with the highest temperature rise. Also in the runs performed from October to December NPD was stable in the RO pilots and no rise could be seen. These runs were performed in periods when temperature was lower. As mentioned above, also the MFS results show growth in periods with warmer feedwater temperature and slow down of growth in periods with colder feedwater temperature.
ii. Start of the brine reuse in IX2: it might be that the brine reuse has an effect on the feedwater quality going to the RO's, f.e. on the type of TOC. No big differences can be seen in the measured components or DOC composition from periods when RO brine was reused to regenerate the IX compared to periods when RO permeate was used. It is less likely that this factor adds to NPD increase because the quality of the feedwater to the RO's does not change a lot, but it can't be excluded with the current info or the MFS unit tests. From the figure above, it can be concluded that the brine reuse is not a factor leading to bio growth when MBR is the feed source.
iii. Type of feedwater source treated: in July the NPD is lowering again from the moment that the feedwater sources were treated separately. It might be that the type of feed source treated leads to bio growth or not. Independent of the quality of the feedwater sources, it can be concluded that biox has a higher biofouling potential because of the higher temperature of the water compared to the mixture or MBR.
iv. The flux: values of NPD are lower for RO-Groot when the flux changed to 18.6LMH. The lower flux might contribute to the NPD decline, but since NPD of the biofouling guard which is still running on a flux of 21LMH, is also stabilizing in July, it seems unlikely that this change in settings causes the NPD to decline. NPD probably just shifts to a new equilibrium after setting change.

It can be stated that there are some minimal problems with bio growth. If values of NPD become too high, a CIP can be performed to successfully restore the NPD. More research is ongoing with the MFS units to find out the reason for this bio growth.

3.4.3 NSP progress and membrane lifetime

The NSP and the MTC progress are plotted for every pilot in Figure 50. A higher value for NSP (12.66%) and conductivity of the permeate (109.7µS/cm) were noticed in the RO-Groot pilot since the start of the project. The values for RO-Groot were much higher than expected. This was caused by leakages in multiple pressure vessels. The leakages were fixed on 13th of April 2021. Afterwards the NSP and conductivity of the product dropped to 0.68% and 8.40µS/cm, which is lower than expected.

After the fix, permeate of RO-Groot, was within acceptable limits. The NSP for each pilot is decreasing during the runtime. This indicates no big damages in any of the membranes in the pilots. NSP seems to follow the MTC. When MTC is lowering more fouling is attached in the pores of the membrane, which causes NSP to lower. More salts are retained by the membrane at low MTC. Therefore NSP is higher after a CIP and is at its lowest before a CIP is performed.

Some membranes of RO-Groot were sent for autopsy on the 27th of July. Delamination of the membranes in an early stage was visible, this could not be seen yet on the membrane of the biofouling guard send in April. Delamination means some backpressure is happening in the pilot during operation or cleaning and can lead to higher salt passage in the future. The effect cannot be seen yet in the NSP, but backpressure strongly decreases the lifetime of the membranes. No observable backpressure was found during operation or newly performed CIP’s.

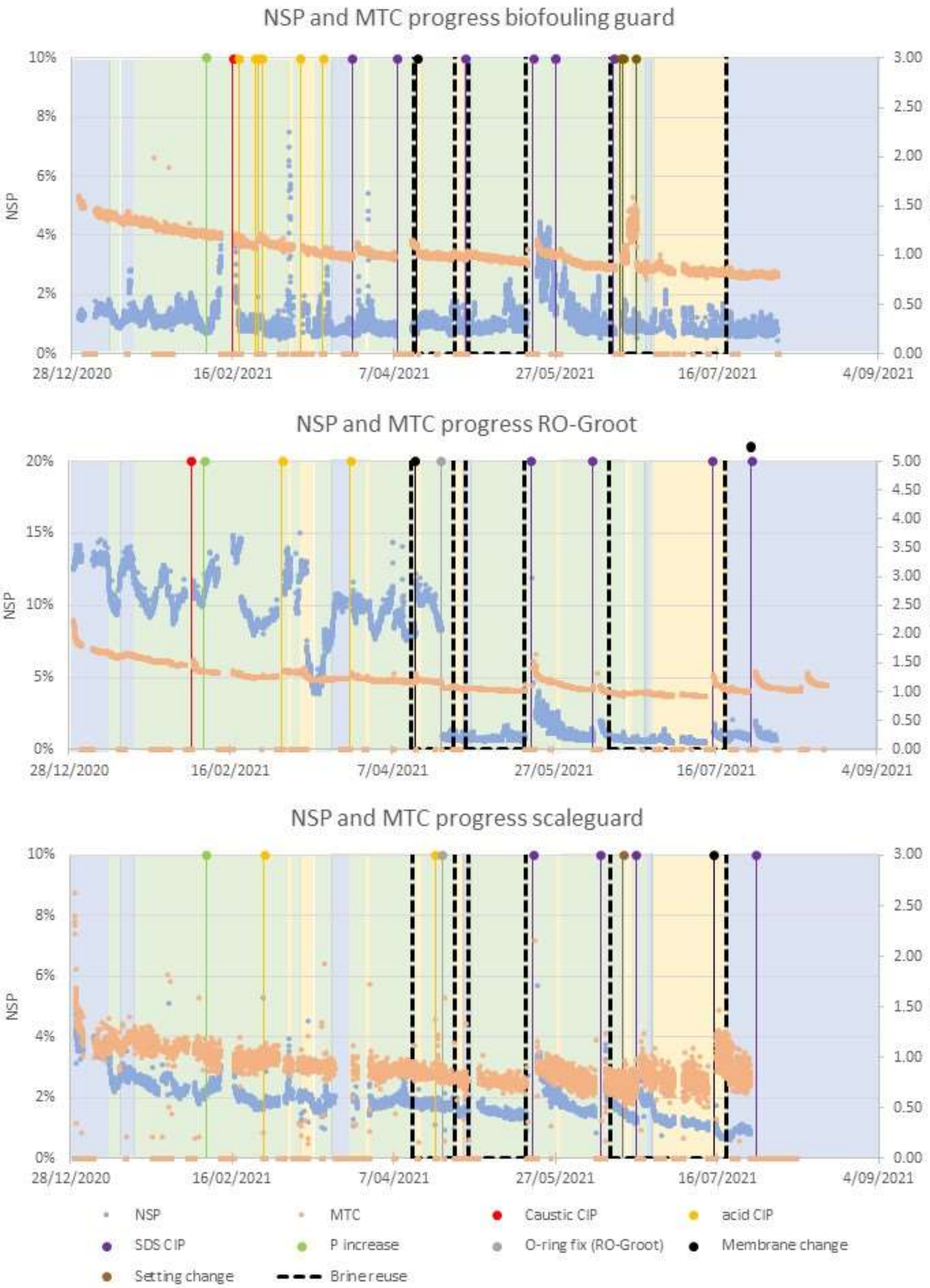


Figure 50: NSP (dark blue) and feedwater MTC (orange) progress for all pilots during CW-UF-IX2-RO run (blue background = MBR as feedwater source; yellow background = biox as feedwater source; green background = mix as feedwater source).

3.4.4 CIP findings

As mentioned above, some fouling and biofouling is attaching on the membranes. In order to remove these foulants, periodic cleaning is needed (Table 49). The MTC could not be restored with the CIPs, while the NPD is able to restore with the CIP's. Therefore, different chemicals were used for cleaning and effect on MTC was quantified. RO permeate was used to clean the RO pilots and flushing happened in the same direction of operation with a flow of 1-2m³/u.

It is clear from that normal caustic (NaOH) CIP's do not help to bring back the MTC, but seem to have a negative effect. Normal acidic cleanings (HCl or oxalic acid) seem to have a minimal effect. MTC increases, but the effect is too small to keep the MTC stable. SDS however seems to restore the MTC partly, but a fast decrease can be noticed. After 10-12days after CIP, the MTC is back at the original level from before the CIP. Next to that a high concentration is needed. The concentration of 0.025% suggested by the manufacturer is too low and at least 10x the amount is needed. Since it is impossible to restore the MTC totally, this means that part of the fouling attached to the membrane is irreversible. The assumed CIP frequency of 1x a month is too little to keep the MTC stable within limits, therefore a CIP frequency of 1x every two weeks is maintained and option 7c is chosen as final CIP strategy. This means circulating with NaOH (pH >12 and T45°C) for 2hours, after 2hours the SDS is added in an excess concentration of 0.8%, which will be lowered in a later stage to find the optimal concentration, and 3hours more of circulation is done with the SDS. Afterwards the pilot and CIP installation is flushed to a neutral pH and conductivity < 50µS/cm. Because of practical reasons the HCl CIP is started afterwards and circulation happens for 12hours during the night. Again a flushing is performed after the acidic CIP until neutral pH and low conductivity are reached. The permeate valve is left open during the CIP and the water going through the permeate valve is recirculated back to the CIP tank.

As can be seen in Figure 45, it was possible to keep the MTC of RO-Groot at a constant level with a flux of 18.6LMH and a CIP frequency of 1x every two weeks.

Remark is that the CIP's are performed semi-automatic. The SDS is added by hand and there were some hardware issues occurring during some CIP's. Because of the hardware issues, the CIP unit went in an error and stopped circulating for an unknown time. This means soaking and cooling down of the CIP liquid instead of circulating at a high temperature. This might be a reason for the lower effect of some CIP's, but cannot be confirmed.

Table 49: Different cleaning strategies used during the project and their effect on the MTC

#	**Type**	**Skid**	**Effect**	**Effect on MTC**
1	NaOH pH12 T35, circulation + soaking (total 3u)	Groot	**-**	5% ↓
2	NaOH pH12 T45, only circulation (3u)	Biofouling guard	**--**	6.7% ↓
3a	HCl pH2, only circulation (3u)	Biofouling guard	**+**	5% ↑
3b	HCl pH2, only circulation (12u)	All	**+**	7% ↑
4	Oxalic acid pH2.2, only circulation (12u)	Scaleguard	**++ / 0**	10% ↑ / 0%
5	HCl pH2 T35, only circulation (12u)	Biofouling guard	**0**	0%
6	NaOH pH12 T45 + 0.1% SDS (5u)	Biofouling guard	**+++ / 0**	15% ↑ / 0%
7a	NaOH pH12 T45 + 0.1% SDS (5u) , followed by HCl CIP pH2 (12u)	Biofouling guard	**++**	13% ↑
7b	NaOH pH12 T45 + 0.8% SDS (5u) , followed by HCl CIP pH2 (12u)	All	**++++**	25-35% ↑
7b	NaOH pH12 T45 + 0.25% SDS (5u) , followed by HCl CIP pH2 (12u)	All	**++ / 0**	3-10% ↑
7c	NaOH pH12 T45 + 0.8% SDS (5u) , followed by HCl CIP pH2 (12u) met permeate valve open	Biofouling guard / scaleguard	**++ / +++**	10% ↑ / 25% ↑

If temperature rises, feed pressures should be lower and therefore also the specific energy use from the pump. The specific energy use and feed pressures are plotted for RO-Groot in **Fout! Verwijzingsbron niet gevonden.**51. It is clear from the graph that the feed pressures and specific energy are rising throughout the run, while the feedwater temperature is rising. The moment SDS CIP's are performed, the feed pressures and specific energy of the pump return to normal values. This means SDS CIP's have a positive effect on feed pressures and energy use of the pump. Overall, it was possible to keep the feed pressure of RO-Groot at a constant level with a flux of 18.6LMH and a CIP frequency of 1x every two weeks.

Figure 51: Top: specific energy use (blue) and temperature (grey) of RO-Groot; bottom: feed pressure (orange) and temperature (grey) of RO-Groot

The estimated dosage f.e. CIP in a CIP tank of 200L is:

- NaOH (33%): 0.350L
- HCl (33%): 0.150L
- SDS (30%): 1.700L

3.4.4.1 Changing frequency of the cartridge filters

There is a cartridge filter of 10µm placed in the biofouling guard and in RO-Groot. The filters never had to be changed during the whole runtime. A picture of the cartridge filter after 5 months of operation is shown in Figure 52. The brown color that is noticeable is situated on the bottom side of the filter. This is probably a flush from the bottom of the feed tank while emptying if no feedwater was available. Especially the cartridge filter from the biofouling guard looks still new and is still good to use. Changing is not needed for at least 5 months of operation.

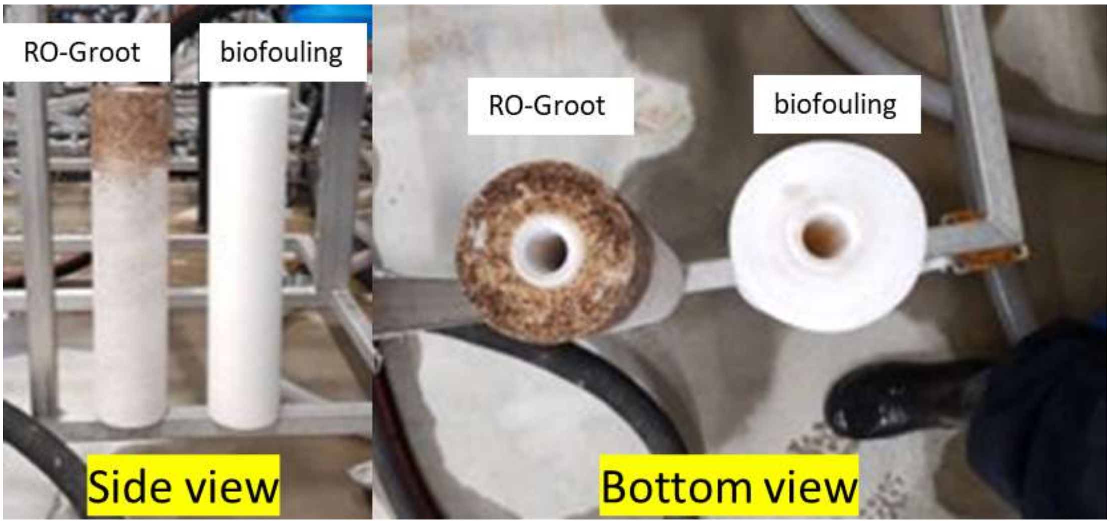


Figure 52: Cartridgefilters of the biofouling guard and RO-Groot after 5 months of operation.

3.4.4.2 Autopsy results and fouling identification

Multiple membranes were send for autopsy during the run, an overview of the analyzed membranes is given below:

- 14/04/2021: biofouling guard membrane was sent to the lab from Dupont in Tarragona (report finished).
- 15/07/2021: scale guard membrane: autopsy performed by ourselves and Dow Terneuzen lab. Samples of the used, an unused membrane and the fouling were sent to the Dow Terneuzen lab to analyse (report in progress).
- 27/07/2021: two membranes of the last array of RO-Groot were send to the lab from Dupont in Tarragona (report in progress).

From the first membranes send, it was clear that the permeate flow was below acceptable limits. The fouling could not be removed with standard NaOH and HCl CIP's and fouling could not be identified. This confirms the little effects of the CIP's performed in the RO pilot research. Standard caustic and acidic CIP's are not enough to remove the fouling and restore the MTC. The element did not show any physical damage.

Therefore it was decided to cut open a second membrane and take some samples for analysis. A brownish, slimy layer could be seen on the PA side of the membrane. This fouling layer followed the pattern of the feed spacer and can be seen in Figure 53. A microscopic analysis of the fouling layer was performed, and the fouling on the membrane was not of a biological nature.

Figure 53: Left: Zoom-in of the fouling layer on the scale guard membrane (15/07/2021). Right: scraping of the fouling on the membrane.

SEM-EDS analysis were performed on the used and unused membrane. A higher nitrogen, oxygen and some aliphatic components could be found on the used membrane compared to the clean membrane. Second, LC-MS was performed after extraction with 100% methanol. A sum of 4-Methyl-1H Benzotriazole and 5-Methyl-1H Benzotriazole was present in a 1000 - 2000 µg/m^2 and 30-60µg/m^2 of benzotriazole was present on the fouled membrane. Afterwards another microscopic analysis was performed on the extracted membrane. Almost no fouling could be seen on the surface of the membrane which indicates that the extraction was successful.

The micro-pollutant research performed in the wetlands (see section **Fout! Verwijzingsbron niet gevonden.**) confirmed benzotriazole and a sum of 4-Methyl-1H Benzotriazole and 5-Methyl-1H Benzotriazole to be present in the same concentration after every treatment step, respectively in a concentration of 2µg/l and 70µg/l. None of these components are removed by the treatment steps prior to the RO.

These results together with the hypothesis in section **Fouling issues** confirm benzotriazoles to be part of the fouling attaching to the RO membranes. The component is used in the Dow company as a cupper corrosion inhibitor end ends up in the biox wastewater stream. In the short future Dow will change its conditioning, eliminating the use of benzotriazoles. It is however not clear if the new conditioning chemical will have a better or worser effect on the fouling of the RO membranes.

More research is being performed to identify possible other foulants.

3.4.4.3 Permeate quality

The removal of all components is between 97.6-99.9.% in the pilots. The quality of the total product and the simulated situation with 85% recovery is given in Table 50. All components are within the limits set in the WSSA except for pH and HCO_3.

Table 50: Measured product quality per pilot and simulated product quality for 85% recovery

	Unit	RO-Groot permeate P90	Scaleguard permeate P90	product simulatie P90	product simulatie max
Temperature	°C	20.46	20.43	20.45	21.06
Turbidity	FTE	<0.025	<0.025	<0.025	<0.025
Suspended solids	mg/l	<1.00	<1.00	<1.00	<1.00
EC25	µS/cm	23.30	96.60	36.39	41.14
pH	pH	6.57	6.56	6.57	7.17
TOC	mg/l C	<0.025	0.12	<0.04	0.05
COD	mg/l O_2	5.30	7.00	5.60	6.18
HCO_3	mg/l HCO_3	10.30	16.60	11.43	12.43
F	mg/l F	<0.01	<0.01	<0.01	<0.01
Cl	mg/l Cl	<2.3	20.40	<5.53	<6.18
SO_4	mg/l SO_4	<0.01	0.08	<0.04	<0.05
SiO_2	mg/l SiO_2	0.05	0.63	0.16	0.19
Si	mg/l Si	0.04	0.40	0.10	0.12
NH_4-N	mg/l N	<0.02	<0.02	<0.02	<0.02
NH_4	mg/l NH_4	<0.03	<0.03	<0.03	<0.03
NO_2-N	mg/l N	<0.00	<0.00	<0.00	<0.00
NO_2	mg/l NO_2	<0.01	<0.01	<0.01	<0.01
NO_3-N	mg/l N	0.17	0.65	0.26	0.26
NO_3	mg/l NO_3	0.76	2.92	1.15	1.16
PO_4-P	mg/l P	<0.01	<0.01	<0.01	<0.01
PO_4	mg/l PO_4	<0.03	<0.03	<0.03	<0.03
TP	mg/l P	<0.0025	<0.0025	<0.0025	<0.0025
Na	mg/l Na	4.33	18.80	6.91	7.72
K	mg/l K	0.49	1.90	0.75	0.86
Ca	mg/l Ca	<0.005	<0.005	<0.005	<0.005
Mg	mg/l Mg	<0.002	<0.002	<0.002	<0.002
Fe	µg/l Fe	<0.4	<0.4	<0.4	<0.4
Fe	mg/l Fe	<0.0004	<0.0004	<0.0004	<0.0004
Mn	mg/l Mn	<0.00005	<0.00005	<0.00005	<0.00005
Al	µg/l Al	<0.5	<0.5	<0.5	<0.5
Ba	µg/l Ba	<0.1	<0.1	<0.1	<0.1
Sr	µg/l Sr	<0.15	<0.15	<0.15	<0.15
ATP	ng/l	<0.50	1.40	<0.66	<0.68

There are some differences between the pilot-scale and the full-scale installation that can affect this product quality.

i. First of all, the membranes used in the pilot have a lower rejection (99.2% versus 99.7%), therefore the quality obtained in the pilots can be somehow worse than for the full-scale. This effect will be small.

ii. A second important factor to mention is the use of Spuikom water as a feed source in the full-scale. This water source is not included in the pilot project and contains a higher amount of calcium, manganese, iron, nitrate, suspended solids, chlorophyll-a and has a somewhat higher turbidity. However the total contribution of the Spuikom water to the total feed source will be only 6%, which is really low. Since all of these components (except for nitrate) are under detection limit in the pilot project, it is not considered as a problem. Nitrate is already present in excess and extra nitrate will not lead to extra biogrowth. The higher amount of nitrate can become a problem if the norm is exceeded by the addition of Spuikom water.

3.4.5 Lower flux (18.6LMH)

Because of the rapid MTC decrease, it was decided to lower the flux to 18.6LMH on 17/06/2021. The lower flux should ensure a less rapid fouling of the membranes and a less rapid decrease of MTC. Positive results of a lower flux on MTC decrease are already obtained in other research projects. Because of reaching the lower limit of the flowmeters in the biofouling guard, it was not possible to obtain good data with the flux of 18.6LMH. Due to bad flow measurements it was decided to place the flux back to 20.6LMH for the biofouling guard, while RO-Groot and the scaleguard continued running on a flux of 18.6LMH (Figure 54).

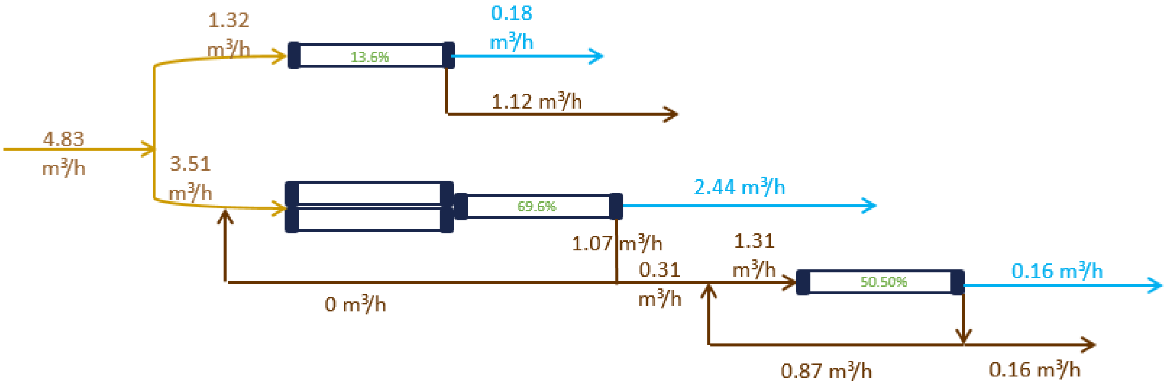


Figure 54: Operational settings for RO pilots from 17/06/2021 until the end of the experiment (flux for RO-Groot and scaleguard = 18.6LMH; flux for biofouling guard = 20.6LMH)

In Table 51 the MTC decline for all three pilots is being looked at in different periods in the research, both periods with higher flux and periods with lower flux. Because CIP's have a big effect on the MTC value, periods between CIP's were selected. No CIP's were performed except for a CIP on the biofouling guard on 29/04/2021 (this CIP did almost have no effect on the MTC) and biweekly CIP on RO-Groot between 21/07/2021 and 16/09/2021.

When looking at the table, it is clear that the most rapid MTC decline is happening right after a new resin was placed in the IX2 pilot (period 2). No difference in MTC decrease per day can be seen for the biofouling guard in the period when IX2 was running with SCAV4 and the mix as feedwater (1) and when IX2 was running with IRA458 and the biox as feedwater (3). It can be said that the change of resins does not influence the performance of the RO pilots after some stabilization period is exceeded. Looking at the RO-Groot and the scale guard, it is clear that during period 1 (high flux) the MTC decrease was 2-3 times faster compared to period 3 (lower flux).

Further, running on MBR slows down the decrease even more. The MTC decrease in the biofouling guards stops, the decrease in the scale guard slows down and for RO-Groot, it was possible to keep the MTC at a certain level with biweekly CIP's. However in between CIP's, a decrease in MTC is noticed.

Table 51: MTC decrease for period with higher flux compared to lower flux periods

	Period looked at	**Pilot**	**Flux (LMH)**	**% MTC decrease /d**	**Remark**
1	Mix/scav4 resin in IX2 (mid April – mid May)	Biofouling guard	20.6	0.24	1 failed CIP
		RO-Groot	21.1	0.65	No CIP's
		Scaleguard	20.6	0.62	No CIP's
2	Mix/start-up IRA458 resin in IX2 (mid May – mid June)	Biofouling guard	20.6	0.81	No CIP's
		RO-Groot	21.1	0.88	No CIP's
		Scaleguard	20.6	0.88	No CIP's
3	Biox/IRA458 resing in IX2 (mid June – mid July)	Biofouling guard	20.6	0.22	No CIP's
		RO-Groot	18.6	0.23	No CIP's
		Scaleguard	18.6	0.32	No CIP's
4	MBR/IRA458 resin in IX2 (mid June – mid September)	Biofouling guard	20.6	0.00	No CIP's
		RO-Groot	18.6	0.00	Biweekly CIP's
		RO-Groot	18.6	0.63	Shorter period in between CIP's
		Scaleguard	18.6	0.09	No CIP's/new membrane/difficult data

It has to be noted that some points have to be taken into account when comparing the data. First of all it is not clear what effect the different feed sources have on the MTC decline. The lower flux was performed on membranes that were already heavily fouled. This might also be a reason that the decline is lower than when the experiment would have been performed with new membranes.

It can be said that a lower flux has a positive effect on the MTC decline, however it is still not possible to keep MTC stable while running on biox with the lower flux. More research is needed to determine the best flux to keep MTC stable on the mixture. Running on MBR seems to stop MTC decrease, this confirms the theory above that the foulant might be present in the biox water.

3.4.6 Conclusion

The biggest problem is the fouling of the RO membranes by the benzotriazole and a sum of 4-Methyl-1H Benzotriazole and 5-Methyl-1H Benzotriazole present in the biox feedwater. This component was indicated as one of the foulants present on the membrane. The fouling is partly irreversible and standard NaOH/HCl CIP's are not sufficient to keep the MTC stable at a high level. Good effects are seen when adding SDS to the caustic cleaning liquid, but the effect of the CIP is gone after 10-14 days. Lowering the flux from 21.1LMH to 18.6 LMH seems to slow down this MTC decrease. Further no bio growth problems are seen in the pilot. In warmer periods there is some biofilm growing in the spacer of the membranes, but NPD values can be restored after performing a CIP.

Overall, the biggest problem is the fouling of the RO membranes by the benzotriazole and a sum of 4-Methyl-1H Benzotriazole and 5-MetFollow-up steps for the RO pilot research are:

i. New membrane in the biofouling guard and use MBR as feed source, followed by new membrane with biox as feed source only to confirm biox as pollutant stream for the membranes.
ii. Lower concentration of SDS during CIP to find optimal one.
iii. Further autopsy on the membranes to identify foulants and cleaning agent.

3.5 General

3.5.1 Comparison of NO_3^- removal by the CW pilot vs. IX pilot

NO_3^- is an anion that can be potentially removed in the brackish water line both by the CW and SBA resin columns. For NO_3^- to be removed during treatment with the CW C dosing is required in the influent stream of the wetlands. For NO_3^- to be removed by the SBA columns of the IX treatment step, NO_3^- will uptake some capacity over other removed ions (SO_4^{2-} and HPO_4^{2-}-P) that results in shorter length of production and therefore more frequent regenerations of the SBA columns and thus higher NaCl consumption.

In order to identify which option of the two is better for the removal NO_3^-, a simple economic comparison between the options was made. Specifically, three scenarios were created, which were:

- Scenario 1; a 20% removal of feed NO_3^- from the CW (no C dosing required)
- Scenario 2; a 40% removal of feed NO_3^- from the CW (C dosing required)
- Scenario 3; a 60% removal of feed NO_3^- from the CW (C dosing required)

The feed anions equivalents to be removed by the SBA columns were calculated for the three scenarios keeping the same content of SO_4^{2-} and $HPO4^{2-}$-P and taking into account the different removals of NO_3^- (Table 52). The cost calculations of required amount of C for the removal NO_3^- by the CW (based on pilot scale) is given in Table 53 for the three scenarios. In Table 54 the cost calculations of the required amount of NaCl for the regeneration and there after the removal of NO_3^- is given for the three scenarios. In both tables the final result is presented as cost (in euro) per Kg NO_3^- removed. In Table 55 the cost for both C dosing and NaCl dosing required for the removal of a Kg NO_3^- by both the CW and IX are summarized.

It can be seen that no extra C dosing is required to further remove NO_3^- in the CW, since this action increases the cost for the removal of one Kg of NO_3^- from 5.82 Euro to 9.17 or 9.79 Euro depending on the required amount of C to be dosed. The main benefit of having further removal of NO_3^- in the CW (by C dosing) would be that the NO_3^- content reaching the RO units would be lower (lower NO_3^- in IX feed => lower NO_3^- in IX product). However, it has already been mentioned in sub-chapter 3.3.1 that N is already in excess for bacterial growth compared to C and P and even higher NO_3^- content in the RO feed won't increase further the bacterial growth potential. Therefore based on both points above it was considered that C dosing in the CW is not required as far as NO_3^- removal is concerned.

Table 52: Anion equivalents to be removed by SBA IX columns in the three scenarios

	Scenario 1	Scenario 2	Scenario 3
Removal by CW of NO_3^- (%)	20	40	60
NO_3^- (feed at 0.71 meq/L)	0.57	0.43	0.29
$HPO4^{2-}$-P	0.04	0.04	0.04
SO_4^{2-}	2.29	2.29	2.29
Feed Anion Equivalents; SO_4^{2-} & $HPO4^{2-}$-P & NO_3^- (meq/L)	2.91	2.77	2.62

Table 53: C dosing cost for the removal of NO_3^- by the CW in the different scenarios

	Scenario 1	Scenario 2	Scenario 3
C Cost (Euro/L C)[16]	0.726		
CW flow (m^3/h)	1.92	1.95	1.98
Required CN ratio	-	3.5	4
Density of C source (g/L C source)	-	650	650
C Dosing (mg/L treated)	-	35	40
C Dosing (L C source/L treated)	-	5.4E-05	6.2E-05
Cost (Euro/L treated)		3.9E-05	4.5E-05
Treated Volume per year (m^3/year)	16846	17081	17322
Cost - C dosing (Euro/year)	0	668	774

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[16] Information obtained by CW pilot engineers.

NO_3^- removed by CW (kg NO_3-N/year)	34	68	104
Cost (Euro)/ kg NO_3-N removed	-	9.77	7.45

Table 54: NaCl dosing cost for the removal of NO_3^- by the IX in the different scenarios

	Scenario 1	Scenario 2	Scenario 3
NaCl Cost (Euro/Kg NaCl)[17]	0.06		
Production Flow (m^3/h)	2.67		
Volume SBA/ batch (m^3/batch)	65	69	72
Production Duration (h)	24.5	25.7	27.1
Batch Duration (h)	28.5	29.7	31.1
Batches/year	770	737	704
Cost - NaCl regeneration (Euro/year)	1404	1344	1284
Gain (Euro/year)	-	60	120
Assumption NO_3^- removal by IX (%)	50	50	50
NO_3^- removed by IX (kg NO_3-N/year)	201	152	102
Cost (Euro)/ kg NO_3-N removed	5.82	5.77	5.72

Table 55: Total cost for the removal of NO_3^- by the CW and the IX in the different scenarios

	Scenario 1	Scenario 2	Scenario 3
NO_3^- removed by IX and CW (kg NO_3-N/year)	241	233	224
Cost (Euro)/ kg NO_3-N removed by CW&IX	5.82	9.17	9.79

3.5.2 BRU in UF effect on IX pilot

The RO concentrate was in some of the experiments used for the backwashes of the UF pilot. It was noted that right after a backwash the EC of the IX feed (UF permeate) was increased for some minutes and then returned to the normal operation value (e.g Figure). This happens because the UF product pipelines after a backwash are filled with RO concentrate.

Two samples were collected right before a backwash (normal operation) and during the peak (after a backwash) to evaluate the effect of the peak on the IX2 pilot operation. The ions concentrations in the two samples are given in Table 56. It can be seen that the increase of the EC can be attributed to the higher concentrations of Na^+, Cl^-, K^+, HCO_3^- and NO_3^- (expected since high content in RO concentrate). In parallel, the target anions (SO_4^{2-} and HPO_4^{2-}) and cations (Ca^{2+} and Mg^{2+}) concentrations were lower in the IX feed during the EC peak (after backwash) compared to the IX feed during normal operation (before backwash). It can be concluded that the peaks in the EC of the IX feed right after a backwash of the UF due to brine re-use do not negatively affect the OC neither of the WAC nor of the SBA resins, since the concentrations of target ions are not higher.

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[17] Information obtained by a DECO full scale process engineer.

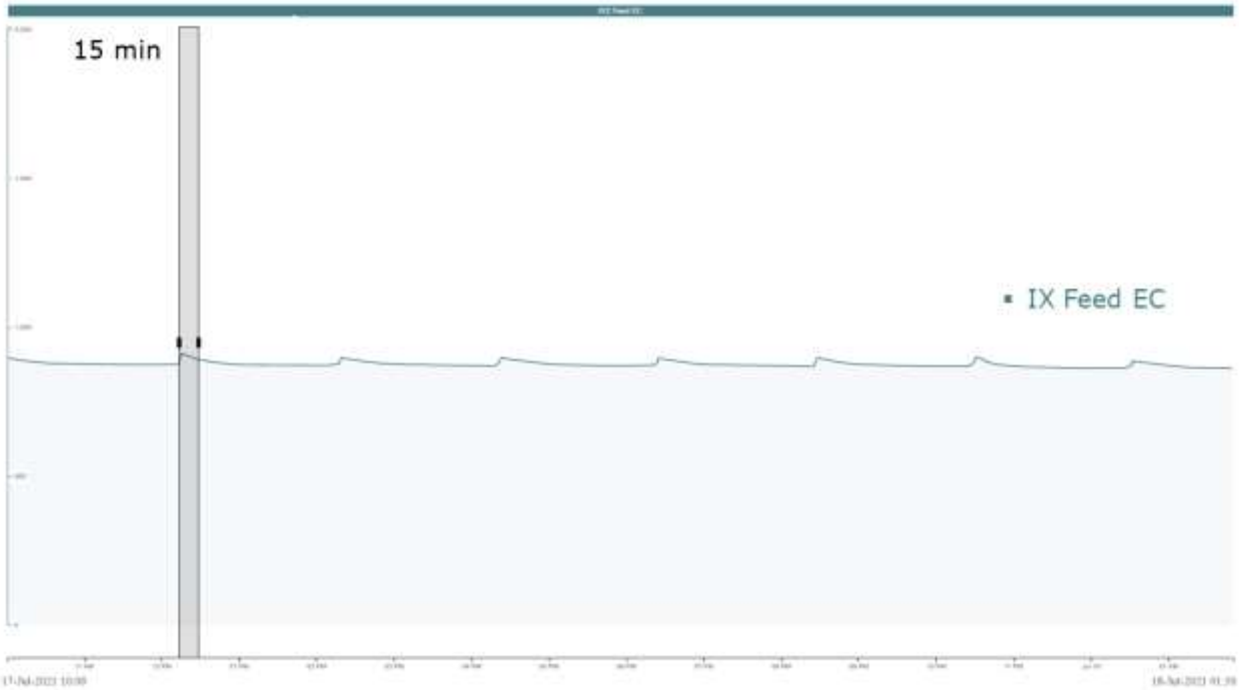


Figure 55: BRU in UF effect in IX Feed EC

Table 56: IX Feed water quality before and after a backwash in the UF pilot

IX Feed/UF permeate	Before backwash (normal operation)	After backwash (during the peak)	Difference (after - before)
EC (µS/cm)	1200	1900	700
	meq/L	meq/L	meq/L
HCO_3^-	3.2	5.4	2.2
Cl^-	5.0	9.3	4.3
SO_4^{2-}	1.15	1.0	-0.15
NO_3^-	0.3	0.6	0.3
HPO_4^{2-}	0.022	0.018	-0.004
Na^+	6.1	13.5	7.4
Ca^{2+}	1.6	1.1	-0.5
Mg^{2+}	0.6	0.4	-0.2
K^+	0.6	0.95	0.35

4. INPUT FOR FULL SCALE DESIGN

4.1 Wetlands

Based on the research results, the following documents were made in which the design is described in more detail:

1. Preliminary design
2. Addendum addressing risks to preliminary design
3. Memo TSS in feedwater

As the design process is still ongoing, some features in the design still need to be discussed within the project group. It is important to note that this predesign is purely meant as a starting point for the final design, which will be made in close cooperation with Rietland BV, Evides Industriewater and Tauw.

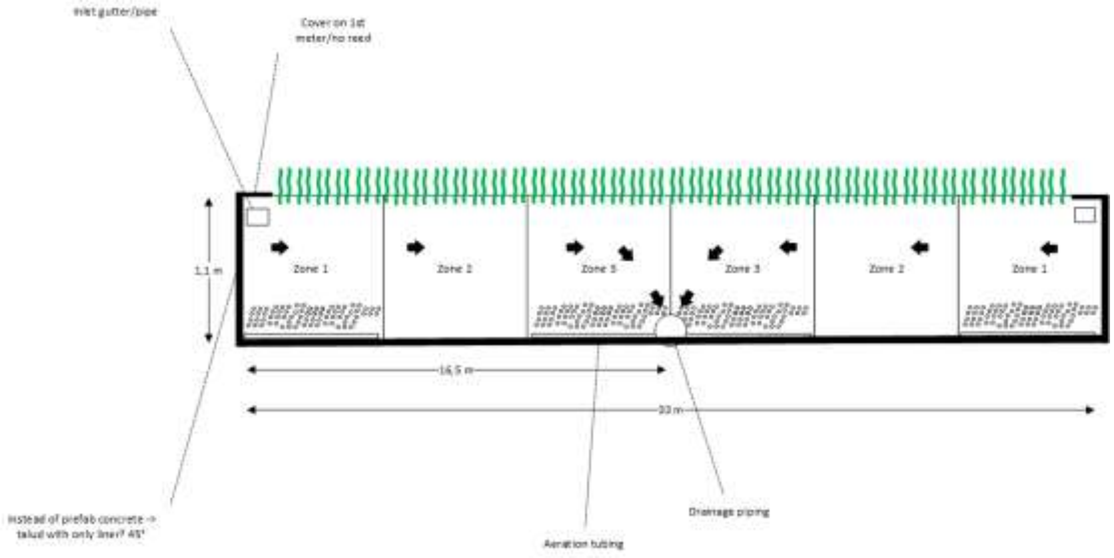
4.1.1 Designated area

The available area as can be seen in fig. 56 has a surface area of 16 hectares and is owned by Dow Terneuzen.

Figure 56: Designated area for full scale wetlands.

4.1.2 Cell design

The wetland is designed with a multitude of similarly dimensioned cells. One cell consists of three zones, of which the first and last zone are aerated. For cost efficiency purposes two cells are locked together, which implies that one singular drainage pipe in the middle can be used. In the current design, the sides have a 90° angle. Another option would be to make use of a 45° angle, thus minimizing costs for concrete. Note that the current dimensions are not related to the 12 hours retention time.



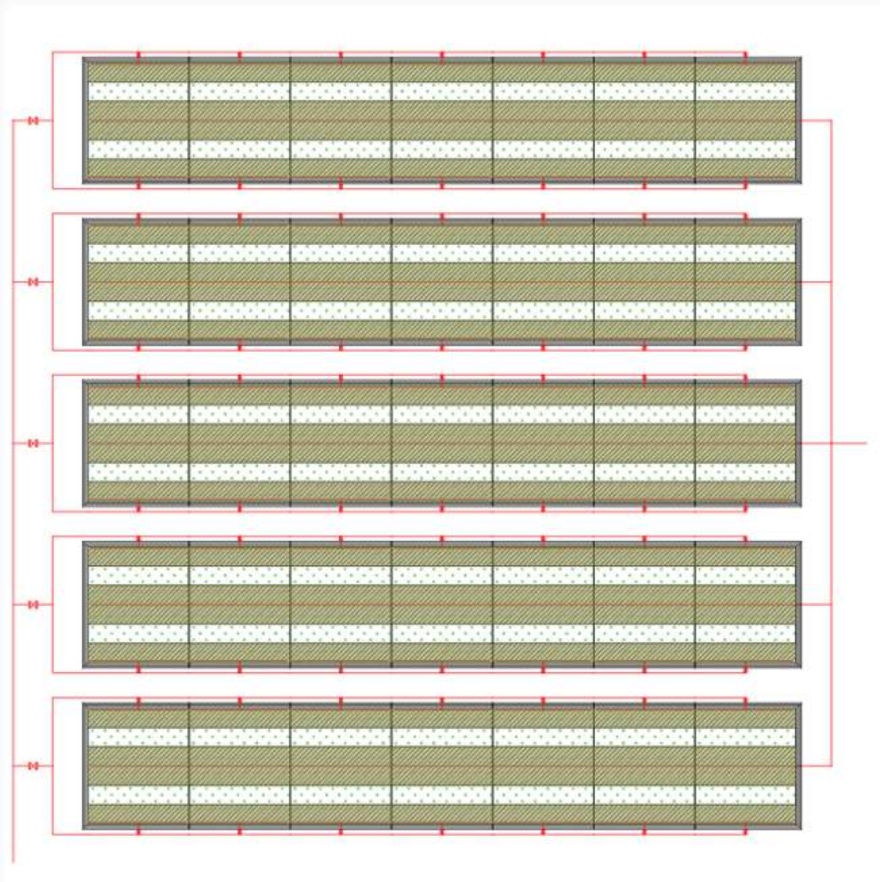
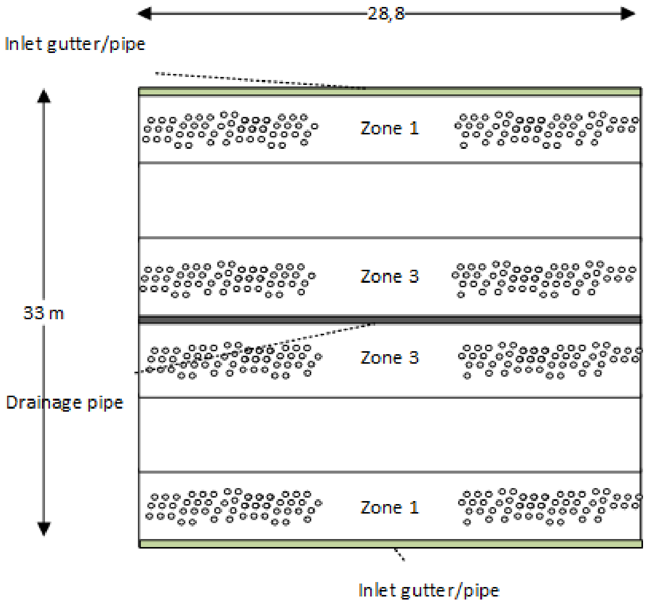


Figure 57 Concept cell design, according to 18 HRT. This should be redesigned to 12 HRT.

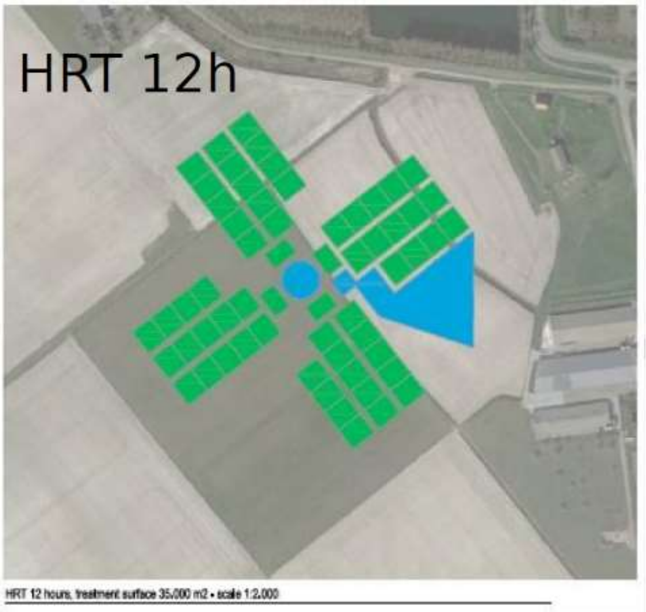


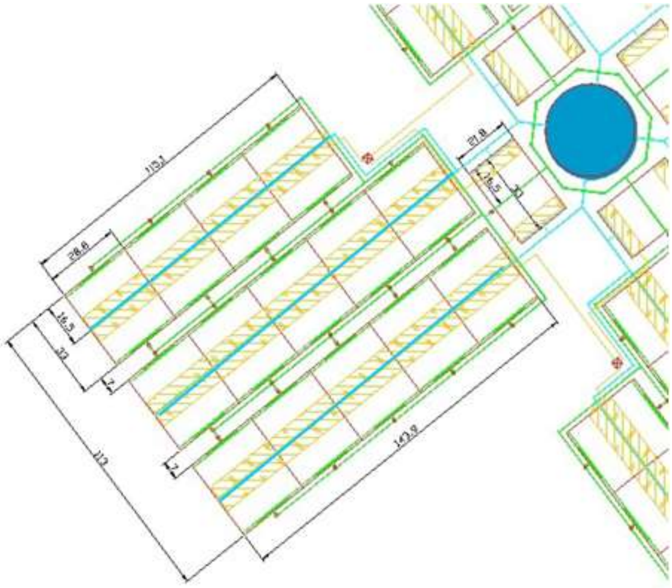
4.1.3 Cell layout

In the predesign made by Rietland, there are two main layouts considered. The rectangular and windmill layouts. The predesign document focuses on the windmill design. However, the individual cells have similar dimensions and treatment performance. Both designs can therefore be considered in the full scale design.

Basic rectangular layout with 12 HRT

Windmill layout with 12 HRT





4.1.4 Construction

Expanded clay aggregates

Special attention should be given to loading the expanded clay into the wetlands. The pilot was loaded using a pressured pipe through which the Argex was blown, causing a portion of the granules to degrade into smaller particles. This is not beneficial for the treatment capacity (faster clogging, more shortcut streams).

4.1.5 Start-up

Start-up constructed wetlands & leaching

During the first 10 months of operation[18], it is highly likely the product water from the wetlands cannot be used as feedwater for the ultrafiltration installation due to elevated iron and sulphate concentrations leaching from the granules. The total volume needed to reduce sulphate and iron concentrations to sufficient levels is estimated for the 3.3 ha to be:

3 months of pilot operation until specs are reached * 29 days per month * 24 hours per day * 900 m^3/h * 80% reduction of leaching measures = 1,5 Mm^3 startup water.

If 200 m^3/h MBR-permeate is available, the startup period will be 7517 hours (313 days, ~10 months).

The effect of leaching is expected to occur longer than the starting of biological activity (especially for NH_4-N-removal) in the wetlands. Options to reduce leaching period and/or volume:

- fill wetland and aerate to heighten concentrations in liquid;
- batchwise startup to minimize water loss;
- pretreat granules prior to loading into wetland (not considered viable after discussion with Argex).

Bisulphite-dosing station during start-up

In the transition period during the startup of the wetland, the MBR-permeate should still be available to be sent to DeCo. Therefore, the MCA-dosing after the MBR should be continued to ensure this backup remains available with similar quality. As a result, the remaining free chlorine in the water that flows through the wetland might be neutralised by adding sodium bisulphite.

Another possibility could be to let the remaining free chlorine into the wetland, as the first months no biological activity is needed yet.

Summer-wintertime startup planning

Optimal planning would be to start the inflow of the wetlands at the beginning of winter, to minimize the risk of water scarcity at Dow (to have the wetlands operational at the start of summer).

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[18] Assuming 200 m^3/h MBR-permeate.

4.1.6 Operation

Feed flows

- Online measurements at RWZI + control valve
- Online measurements at spuikom + control valve
- Online measurements at Biox + control vale
- Control on feed flow per cell, or per

Quality

Weekly/daily/online measurements in-out on:

- TOC/COD
- NH_4-N
- NO_3-N
- SO_4
- PO_4-P
- SiO_2
- Fe
- EC

Aeration

- Control over aeration in zone 1 and 3 per cell.

Buffer capacity & quantity regulation

- Level sensors connected to pumping station level and control valves at RWZI, Spuikom, Biox.
- Impact with heavy rainfall, negligible (per year approx. 24.000 m^3 at 700 mm/y on 3,3 ha)
- Total buffer capacity available: 20 cm. Regular height would be 1,1 m. If the water level can drop 20 cm, that will give (20 cm * 3,3 ha * 0,7 volume Argex) 4620 m^3 buffer capacity.
- Impact of heavy rainfall on product water quality is regarded as negligible due to quality of rainwater.

Maintenance

- Harvesting 1/year in February.
- Removing trees to keep liner intact.
- Weekly round to check inlet & outlet points, check for clogging.
- Possible removal of sludge accumulated in inlet zone.

4.1.7 Decommissioning

At the end of the operation, the wetland can be decommissioned (or the contract prolonged). The main aspect at the end-of-life of the wetlands will be the reuse of expanded clay aggregates. The volume available will be approximately 3,3 ha * 1,1 m = 36.300 m^3 expanded clay aggregates.

The top 30-50 cm will be less reusable as product by a company like Argex due to the reed roots containing more organic material, so a valid estimation would be that around 60% of the granules might be reused. The top layer could still be used for other purposes, but these are not investigated in this research. Total amount to be reused as a direct expanded clay aggregate product will therefore be 21.780 m^3. The surplus will need to be removed in another way. Results from Tauw and Argex, as indicated in this report, show that granules can be reused after a use of two years.

4.2 Ultrafiltration

Treating effluent of the MBR and the Biox directly with UF was considered the worst-case scenario for the operation of the UF. In the base-case scenario the UF feedwater would be pre-treated by DLF and BACF, which will probably resolve the issue of biological growth. The worst case, direct treatment, will result in lower fluxes and shorter filtration times. Fluxes higher than 60lmh and filtration times longer than 15 minutes are not advised. CEB's should be performed twice daily with special focus on chemicals that prevent biological growth (NaOH and NaOCl).

With the **constructed wetland** as a pre-treatment a **flux of 60 lmh and a filtration time of 60 minutes is advised**. CEB's can be applied once a day with the pattern (t24)citric > (t48) citric > (t72) caustic or the preferred pattern (t24) caustic > (t48) caustic > (t72) citric. The reason for the preferred second pattern is that the effect of a caustic CEB is often greater than a citric CEB, resulting in a permeability that is less variable. Further, the advised regime for backwashes and CEB's would be as mentioned in chapter 2.3.2, Table 9.

The limits of the UF have not been found yet with the constructed wetland as a pre-treatment, which means that the indicated settings in this paragraph are **a solid start to operate the UF on full-scale**. In the meantime tests with the UF are still continuing in order to find the limits of the system with this pre-treatment.

With the brine reuse it is advised to follow the performance of the backwashes (pressures or backwash TMP to indicate arising problems early) next to permeability. It is also advised to have a permeate dump after a backwash (+/-10 seconds) so that the remaining brine salts do not end up in the produced water of the UF. A forward flush will remove the brine salts on the feed side of the membrane, but not on the permeate side. It is also advised to always keep UF permeate as a back-up for backwashes.

4.3 Ion-exchange (softener-scavenger)

4.3.1 General inputs and recommendations for full scale

The recommendations and points of attention for the full-scale design based on the research on the WAC and SBA resins in IX pilots are presented below. It must be pointed out that in all experiments with IX2 the two resins columns were treated as one unit. This means that both resins columns are regenerated and are sent back in production at the same time. The main benefit from treating the two resins as a unit is that the same water can be used for both resins during some steps of the regeneration (backwash, displacement and prewash). A disadvantage of treating both resins as a unit is that in case one of the two resins beds is exhausted earlier than the other resin (for instance because of varying feedwater quality), the latter also has to be regenerated even though it was not exhausted yet. Thus, the chemical consumption for one of the two is higher than it could have been. To avoid this issue, an option would be to treat WAC resin and SBA resin columns as individual units. For this though extra water storing infrastructures are needed. The extra required storage tanks would be (i) for the softened water (after WAC), (ii) for the backwash water, (iii) for the displacement water and (iv) for the prewash water. Possibly the storage tank for the backwash water and the displacement water could be the same. But, it is uncertain if the use of stored (therefore mixed) water for the regeneration will have a negative effect on the regeneration performance and the subsequent OC, since all results from IX2 experiments are based on WAC and SBA resin columns treated as unit where the water used for the regeneration in both column was in plug flow. To avoid any uncertainties in the full scale operation the advice of the research team would be to design the WAC and the SBA pilot as one unit, since it was tested in such a way in IX2 pilot.

WAC Resin: It is proposed for the full-scale design to use the Amberlite HPR8300 WAC resin.

SBA Resin: It is proposed for the full-scale design to use the Amberlite IRA458 SBA resin.

Production and Regeneration Settings: In IX2 experiments, the production was downward (first through the WAC resin column and the trough the SBA resin column) and the regeneration was upward. The reverse direction in both production and regeneration is possible as long as the system remains counter-current. But, it must be kept in mind that it was not tested in IX2 pilot. In case of an upward regeneration the SBA resin bed should be kept packed during regeneration.

The flows used in the IX2 experiment were 11 BV/h for the WAC in Na form and 7 BV/h for SBA (given as reference). The velocity in the IX2 experiment was 20 m/h for the WAC and 10 m/h for SBA (given as reference).

It must be pointed out that there are some differences between the proposed regeneration settings for the full scale and the pre-liminary design (presented in sub-chapter 2.2.3). But, the proposed regeneration is the one tested with IX2 pilot experiments and is advised to be followed for the full scale design. Therefore, the regeneration of the WAC and the SBA resins that is proposed for the full scale consists of the 8 steps given in Table 57. The regeneration flowrates as well as each step's duration based on the IX2 research are also given as reference. There is some flexibility to deviate from the proposed points (e.g. different % of chemicals, flow directions, contact time etc.). However, some points to be taken into account are given below:

- Avoid the combined dosing of NaOH and NaCl, which was proposed in the pre-liminary design, since IX2 experimental results were not promising. A lot of uncertainties about it remain. If there is still an interest in it for the full scale further research is needed to find out what can be changed so as to avoid capacity losses and just benefit from the lower time and potentially lower amount of water required for the regeneration.
- The NaOH dosing (also when separate) should be passed only though the WAC resin column and not the SBA resin column.
- A minimum duration of about 20 min should be kept for the chemical dosing steps.
- Instead of prewash with demin water (or IX product water) as a final step of the regeneration, a dump with feed water could be chosen that will cost some OC, but no product water.

The stoichiometry for HCl dosing over passed equivalents that was tried with IX2 was as low as 140% HCl. Even a lower value at 105% HCl over the past equivalents is considered possible (based on IX1 experiments) but further research with IX2 is required. The NaOH is proposed to be about 40% of the HCl dosing (≈60% over passed equivalents). In this way the pH after the WAC columns and before the SBA columns in the follow up production can be maintained in lower levels (≈ 7.5 to 6.5) as it was found to be beneficial for the SBA performance. The exact number of 40% is depending on the feed water composition (total hardness vs alkalinity). Some parts of the year even lower dosages might be possible, but if this reduction in chemical consumption is desired, the ionic composition needs to be checked at a more detailed level (to be able to act accordingly in real-time). The effect on the WAC OC from the lower NaOH dosing compared to the HCl was not researched. A negative effect is not expected, but further research to verify it should be performed operating only the WAC resin column with IX2 pilot.

The regeneration of the SBA resin is proposed to be based on a regeneration level of 80 gr NaCl/Lr in the full-scale design. The possibility to regenerate IRA458 with 60 gr NaCl/Lr needs to be further researched with IX2 pilot.

Table 57: Proposed regeneration steps for IX

	Regeneration steps	Through (and in the given order)	Direction	Flow rate (BV/h) over WAC*/SBA	≈Duration (h)	BRU
1	Backwash	SBA and WAC	Upward	6/3.5	0.5	Yes
2	4% HCl dosing	WAC	Downward	4.5/-	0.5	Yes
3	Displacement	WAC	Downward	4.5/-	0.3	Yes
4	2.5% NaOH dosing	WAC	Upward	6.0/-	0.25	Yes
5	5% NaCl dosing	SBA	Upward	-/3.5	0.3	Yes
6	Displacement	WAC and SBA	Upward	-/4.5	1	Yes
7	Settling/bed rest	-	-	-/-	0.17	-
8	Prewash	WAC and SBA	Downward	7/4.5	0.5	No
	Total	-	-	-	3.52	
* Na form						

Brine re-use: It was concluded that brine re-use for the regeneration of the IX unit is feasible as far as the achieved OC of SBA resins and the product water quality is concerned. The IX unit recovery is increased based on IX2 research with IRA458 from 94% to 99%. The regeneration steps that can take place with RO concentrate (brine re-use) are the backwash (1), the HCl dosing (2), the HCl displacement (3), the NaOH dosing (4), the NaCl dosing (5) and the displacement (6). Thus, the only step in which RO permeate or IX product water should be used is the prewash (8, or IX feed in case of a dump).

The effect of brine re-use on the OC of the WAC resin was not researched with the IX2 pilot. A negative effect on is not expected, but further research to verify it should be performed operating only the WAC resin column with IX2 pilot.

Exhaustion point:

For SBA; It is proposed to control the SBA resins production based on HPO_4^{2-}-P measurements in the product water (measured by an online analyzer) following the rule "to stop production at product P = feed P/2 ≈ 0.3 mg P/L for the mixed stream". In this way, the throughput per batch is higher but in the same time a buffer-time is provided before SO_4^{2-} leakage is noted in the product water.

For WAC; It is proposed to control the WAC resins production based on TH measurements in the product water (measured by an online analyzer) following the rule "to stop production when TH is above 0.01 mmol/L (low detection limit of analyzer)."

Two different exhaustion points are given for each type of resin, but the production of the WAC resin will follow the exhaustion point of the SBA resin and vice versa depending on which one is exhausted first since both the WAC and the SBA resin columns are treated as a unit.

A few notes related to **brine re-use** and **exhaustion points** topics:

- In the full-scale an increase in the recovery of the IX unit due to brine re-use is certain but the percentages might differ from those achieved with IX2 pilot (e.g. due to different ratio WAC vs SBA resin volume).
- A question that couldn't be addressed with the pilot research is whether or not the high TOC content of the RO concentrate (on average 11 mg C/L) would cause organic fouling on the resins in the long-term due to the brine re-use.
- Running based on the previous mentioned rule will result in higher NO_3^- concentrations in IX product. However, this is acceptable, since N is already in excess in IX product compared to P and C and more N won't increase further the bacterial growth potential.
- To avoid SO_4^{2-} leakage in the product water a smooth pattern in regeneration sequence is required and therefore the regeneration patterns should be closely monitored for issues/ delays (e.g. due to lack of water/ chemicals, malfunction of pumps etc).

- A possible point that the regeneration patterns can be disturbed and therefore SO_4^{2-} leakage can be noted is a malfunction of the HPO_4^{2-}-P analyzers that based on which the production time is controlled.
- Another possible point of SO_4^{2-} leakage is after prolonged stops of the column operation (e.g. due to lack of feed water, malfunction of a pump or other technical issue). When this happened during IX2 pilot experiments it was noted that the OC was negatively affected (feed water standing still and an equilibrium between the resins and the water was reached).
- Another point of attention is in case the feed water of the whole water treatment line is just BIOX instead of the mixed stream. In this case, the 0.3 mg P/L used as the exhaustion point is not equal to the feed P/2, but equal to the feed and the buffer time mention above is not available any more. In IX2 pilot experiments, the value was not adjusted in the run with only BIOX and still no SO_4^{2-} leakage issues were noted due to also good pattern in regeneration (luck that no other issues occurred at the same time to disturb regenerations is a big factor here). To be more sure that SO_4^{2-} leakage is avoided, an option is that the exhaustion point in the software might need to be adjusted accordingly (e.g. at 0.2 mg P/L). In MBR this issue does not exist since the 0.3 mg P/L is about the feed P/3.
- An online HPO_4^{2-}-P analyzers in the feed water is also considered useful in order to provide information in cases where HPO_4^{2-}-P in feed water is unexpected low (e.g. during the experimental period with IX2 there was a time where the feed HPO_4^{2-}-P was 0.15 mg P/L).
  Possible option: Analyzer AMI Phosphate from SWAN, link:
  https://www.swan.ch/Catalog/en/ProductDetail.aspx?subchapter=Chapter_Shop&prdtGroup=Grp_Shop_Analyzer&prdtSubGroup=Grp_Shop_Analyzer_PO4&prdtName=A-25.421.100.0
- In the event of SO_4^{2-} leakage in IX product, a backup plan needs to be considered in the full-scale design in order temporarily stop brine re-use (RO concentrate) and use as an alternative the RO permeate up until SO_4^{2-} is not detected in IX product (<5 mg/L) and RO concentrate (<10 mg/L).
- Based on the previous point, the SO_4^{2-} content of the IX product and the RO concentrate should be monitored.
  A possible option: EZ1036 Sulphate analyzer from Hach with a range of 10-40 mg/L that can accept multiple streams, link:
  https://www.hach.com/ez-series-analyzers/ez-series-sulphate-analyzers/family?productCategoryId=55069943304
  Moreover, for the IX product in case of HPO_4^{2-}-P leakage is detected in IX product (=> expected SO_4^{2-} leakage) or in case SO_4^{2-} is detected in the RO concentrate based on online analyzers, then the SO_4^{2-} content in IX product can be checked fast with "SulfaVer® 4 SulfateReagent Powder Pillows" from Hach, link:
  https://www.hach.com/sulfaver-4-sulfate-reagent-powder-pillows-10-ml-pk-100/product?id=7640197886
- Also, a backup plan is needed to be considered in the full-scale design in order temporarily stop brine re-use (RO concentrate) for the regeneration and use as an alternative stored demin water in case the RO operation faces issues and the RO concentrate produced quantities are not sufficient.

Operational Capacity (OC) of the SBA: The OC expected for IRA458 is **0.600** eq/Lr based on 100% removal of SO_4^{2-}, 85% removal HPO_4^{2-} and 0% removal NO_3^{2-} in cased of the mixed 50/50 BIOX and MBR stream as feed, brine re-use and 80 gr NaCl/Lr dosing. However, differences in the OC of the SBA were noted when partially MBR or BIOX were used as feed water. The worst case was noted when MBR was the feed water of the brackish water line. Specifically, the OC expected for IRA458 is **0.423** eq/Lr based on 100% removal of SO_4^{2-}, 80% removal HPO_4^{2-} and 8.5% removal NO_3^{2-} in cased of MBR as feed and 80 gr NaCl/Lr dosing. This value is expected to be somewhat higher if brine re-use is also applied.

Here a design decision must be made on whether or not the dimensioning of the SBA vessels should be based on the mixed stream or the MBR values. The research team proposes the worst case to be followed, therefore the MBR. In this way, the full-scale reliability is ensured when the only available source water is MBR. And when the mixed stream is used (majority of the operational period), the throughput of the SBA resins will be higher than that of the design (operational expenses lower).

Please note that in order to calculate the required volumes of SBA resin based on the above given OCs the correct removal factors (as noted above) for the target anions should be used in the feed water quality.

Operational Capacity (OC) of the WAC: The outcome of the research for the WAC resin with IX1 resulted in an OC of 3.80 eq/Lr in H form with a dosing of 105%HCl and NaOH over the TVC. Theses result needs to be verified for the full-scale design with further research in IX2 pilot, since a WAVE run was found to be insufficient as mention in sub-chapter 3.3.1. Also, in case of lower dosing as proposed above (105%HCl and 45%NaOH), if the same OC can be achieved should be checked with IX2 pilot experiments operating only the WAC resin columns.

Chemical consumption: The expected chemical consumption of HCl, NaOH and NaCl per m^3 of water produced based on OC of 0.6 eq/Lr SBA and 3.8 eq/Lr WAC and the average target cations and anions content of the mixed stream is given in Table 58. The NaCl value is based on the IX2 research, while the HCl and NaOH are estimations based on the expected OC in the proposed dosings.

Table 58: Chemical consumptions per volume of water produced expectations for IX

Chemical dosing per volume of produced water	Mixed Stream
HCl dosing (g/m^3)	170
NaOH dosing (g/m^3)	75
NaCl dosing (g/m^3)	275

Expected product water quality: The expected product water quality and the subsequent removals for the main parameters of interest after treatment with the WAC and the SBA resins are given in Table 59 (assuming the mixed stream as feed water). The EC is expected to about the same (small insignificant increase, due to exchange for the more mobile Na$^+$ and Cl$^-$ ions).

Table 59: Product water quality and removals expectations after treatment with IX

Parameter	Unit	Product	Removal (%)
TOC	mg/L C	3	65
SO_4^{2-}	mg/L	<5	98
NO_3^-	mg/L	26	0
HPO_4^{2-}-P	mg/L P	0.1	85
Ca^{2+}	mg/L	<0.2	99
Mg^{2+}	mg/L	<0.1	99
Fe^{3+}	mg/L	<0.005	90
pH	-	7.5-8	-

4.3.2 Monitoring suggestions

Based on the previous suggestions for the full-scale it is clear that some water quality parameters need to be monitored with online transmitters and analyzers.

Required transmitters:

1) pH transmitters are required to be placed (i) after the WAC column and before the SBA column and (ii) after the SBA column of each line
2) EC transmitters are required to be placed (i) in the IX feed water, (ii) after the WAC column and before the SBA column and (ii) after the SBA column of each line
3) A temperature transmitter is required in the IX feed water

The pH, EC and temperature transmitters are necessary because they provide an overall idea on how the prosses is progressing. Also, they can provide insights in case of issues with the operation or unexpected results. A specific application of the pH transmitters is that they provide the option to check the pH between the WAC and SBA columns and verify if the NaOH dosing during regeneration needs to be adjusted.

Required analyzers in the feed water:

1) TH analyzers – range = 1 to 4 mmol/L, Option: Testomat ECO from Heyl, link: https://www.heylneomeris.shop/en/Testomat-ECO/100122
2) SO_4^{2-} analyzer – range = 80 to 150 mg/L à option: EZ4039 Sulphate analyzer from Hach, link: https://www.hach.com/ez-series-analyzers/ez-series-sulphate-analyzers/family?productCategoryId=55069943304
3) HPO_4^{2-}-P analyzer – range = 0.1 to 3 à option: Analyzer AMI Phosphate from SWAN, link: https://www.swan.ch/Catalog/en/ProductDetail.aspx?subchapter=Chapter_Shop&prdtGroup=Grp_Shop_Analyzer&prdtSubGroup=Grp_Shop_Analyzer_PO4&prdtName=A-25.421.100.0
4) NO_3^- analyzer – range = 5 to 60 mg/L à option: UV400 NO_3^- analyzer by Tethys, link: http://www.tethys-instruments.com/UV400.aspx

Required analyzers in the product water:

1) TH analyzers – range = 0.01 to 0.09 mmol/L, Option: Testomat ECO from Heyl, link: https://www.heylneomeris.shop/en/Testomat-ECO/100122
2) HPO_4^{2-}-P analyzer – range = 0.02 to 0.3 à option: Analyzer AMI Phosphate from SWAN, link: https://www.swan.ch/Catalog/en/ProductDetail.aspx?subchapter=Chapter_Shop&prdtGroup=Grp_Shop_Analyzer&prdtSubGroup=Grp_Shop_Analyzer_PO4&prdtName=A-25.421.100.0
3) NO_3^- analyzer – range = 5 to 60 mg/L à option: UV400 NO_3^- analyzer by Tethys, link: http://www.tethys-instruments.com/UV400.aspx

Required analyzer in the RO concentrate:

1) SO_4^{2-} analyzer – range = 10 to 40 mg/L à option: EZ1036 Sulphate analyzer from Hach, link: https://www.hach.com/ez-series-analyzers/ez-series-sulphate-analyzers/family?productCategoryId=55069943304

The analyzers should be selected based on the quality of the water to be analyzed (feed, product and RO concentrate). Some options are given for each analyzer above. These are just suggestions. Other analyzers could be chosen too. The signal of all analyzers should be connected to the software of the pilot and thereafter to the PI system of Evides. The purpose of the analyzers proposed is given below:

1) The analyzer to control the WAC production based on the exhaustion point (mentioned earlier) will be the TH one.
2) The OC of the WAC columns can be calculated at any time based on the TH measurements from the TH analyzer in the feed and the throughput of each column.
3) The TH analyzer in the product is to also check the product water quality, in case of off-spec water scaling inside the RO system occurs;
4) The production of the SBA would be control based on the exhaustion point (mentioned earlier) with HPO_4^{2-}-P analyzer.
5) The OC of the SBA columns can be calculated at any time based on (i) the SO_4^{2-} measurements from the analyzer in the feed, (ii) the NO_3^- measurements from the analyzer in the feed and in product, (iii) the HPO_4^{2-} measurements from the analyzer in the feed and in product and (iv) the throughput of each column.
6) The NO_3^- and HPO_4^{2-} measurements are there to check the product water quality.
7) The SO_4^{2-} analyzer in the RO concentrate is required to automatically activate and deactivate the brine re-use for the regeneration in case SO_4^{2-} leak in IX product results in concentrations >10 mg/L in the RO concentrate. Optionally, these analyzers can be designed to accept both the RO concentrate and the IX product alternately (in rotation).

One analyzer of each is enough for the IX feed stream and for the RO concentrate stream. However, for the product side if the IX system consists of 6 identical and parallel lines, there are two suggestions for the full-scale design:

Suggestion 1: One analyzer per 3 lines
The analyzers will accept the mixed stream of 3 lines and when the set point has been reached (e.g. exhaustion point for SBA HPO_4^{2-} equal to 0.3 mg/L), the longest running set of the 3 will be sent in regeneration. In this way the contribution of each set to the mixed stream that is sent to the analyzers is 1/3 and a similar situation with the IX2 operation will be created. The production of each individual set will be able to continue above the set point as long as the mixed stream of the 3 lines is within the acceptable limits.

Suggestion 2: One analyzer for all 6 lines
The analyzers will accept the mixed stream of 6 lines and when the set point has been reached (e.g. exhaustion point for SBA HPO_4^{2-} equal to 0.3 mg/L), the longest running set of the 6 will be sent in regeneration. In this way the contribution of each set to the mixed stream that is sent to the analyzers is 1/6. The production of each individual set will be able to continue above the set point (even more than in suggestion 1) as long as the mixed stream of the 6 lines is within the acceptable limits.

An underlying drawback of suggestion 2 is that in case of an issue with the control system then all 6 production lines are affected, while with suggestion 1 the problem is limited to the half of the production capacity of the IX system. However, suggestion 1 is related to higher CAPEX and OPEX (maintenance, monitoring).

The use of one from each suggested analyzers per IX line is also an option that will result in more accurate monitoring of each line. In this case, a new exhaustion point to allow the production of each individual set to be similar with that in suggestion 1(IX2 pilot research situation) is required to be identified.

The analyzers accuracy should be monitored. A logbook with the values that the analyzers gives and the values measured with Hach kits at the same time in grab samples should be kept. The accuracy checks are proposed to be performed twice per week (spread). Moreover, depending on the needs of each analyzer a schedule should be created that includes (i) cleaning chemicals and reagents refill, (ii) checks on the analyzers sensors, pumps, flow cells etc. and (iii) maintenance frequency by the supplier.

Some options in case that many analyzers are not possible to be included in the design due to budget limitations are given below:

- In case a NO_3^- analyzer is to be placed in the effluent of the wetlands, then the same measurements can be used for IX needs (no need for another analyzer after the UF unit), but the signal needs to be sent to IX software.
- The NO_3^- analyzers (one feed and two in product) are proposed to be included in the monitoring system to provide extra info about the NO_3^- removal at any time and to provide a better insight in cases where the system does not operate as expected as well as to give the option to control SBA resin’s production based on NO_3^- exhaustion and therefore results in no HPO_4^{2-}-P in product. However, their use is not crucial and could be skipped in the full-scale design both from the feed and the product streams. In that case some measurements with Hach kits of the NO_3^- concentration in the feed water a couple of times per week would be useful. This is a risk assessment.
- The use of a SO_4^- analyzer in the IX feed line could be replaced with daily SO_4^- measurements with Hach kits. But, this entails some assumptions as far as the feed equivalents being treated by IX, since a daily measurement on a grab sample is just for one instant. More uncertainties exist especially during the weekend where no measurements are at taken place. Here, it must be pointed out that a relationship between EC and the target anions (SO_4^{2-} and HPO_4^{2-}-P) in the feed water (MBR and BIOX) was searched and it was found that there is none.

Finally, weekly full analyses of the IX feed and IX product water samples are proposed to be arranged with AQZ.

Note: It is considered certain and thus is not discussed in detail that the design will include pressure and flow transmitters in points required for the hydraulic operation and the automation of the pilot.

4.3.3 Summary of points for further research (September to December 2021)

As it has been mentioned before, the operation of the WAC resins has not been researched in detail with pilot experiments. Experiments with IX2 pilot operating only the WAC resin column are required to verify expectations mentioned in the whole report. Specifically, the following questions should be answered when a dosing of 105%HCl and 45%NaOH over the passed equivalents and brine re-use are the regeneration settings of the WAC resin:

"Can an OC of at least 3.80 eq/Lr in H form (assumed for full-scale, achieved in IX1 experiments) be achieved when lower in total dosing, lower NaOH dosing compared to the HCl dosing and brine re-use are applied? And if not, how much lower is the OC with these settings?"

The above research about WAC resin is considered one set of 3 experiments and is expected to need about two months. Another experiment that is required to be performed with IX2 pilot is about the option to regenerate the IRA458 SBA resin with 60 gr NaCl/Lr (25% lower chemical use) without significant OC losses while the brine re-use is on). For this experiment the expected time required is about a month and it should be research before the WAC resins experiments based on the current status of the IX2 pilot.

More research is required about the combined dosing of NaOH and NaCl. This set of experiments should be performed last (or at least after the IRA458 SBA resin with 60 gr NaCl/Lr experiment), since it is considered a potential crash test of the SBA resins (as found with IX2 research with SCAV4). Some options relevant to combined dosing to be researched are the following:

1. A combined dosing could be tested but with longer displacement of the WAC columns after the HCl dosing and lower dosing of NaOH equivalents compared to HCl (<<40%). Also, how much more water is needed for the better displacement compared to how much water is saved from the combined dosing should be investigated.
2. Another option could be to inject the NaOH and NaCl first trough the SBA column and then sent it to the WAC column. In that case the plug-flow extra displacement does take place (though the WAC) column and precipitation is unlikely since any CO_3^-, SO_4^{2-} or HPO_4^{2-}, do no longer have Mg^{2+} or Ca^{2+} to precipitate with (since they are washed out upwards).
3. Check possible special treatments in case of reduced OC to recover it to original values. In the resin analyses report reference values to new resins were found while the same resin in pilot showed a reduced OC. Apparently using some special treatment the OC could be recovered.

The priority order for these sets of experiments with IX2 is based on the described logic. In case the full-scale design needs are different, changes in priority order are possible, but might impact the effectiveness of some of the research.

4.4 Reverse-osmosis

4.4.1 Operation

A continuous flux of 21 lmh for this feedwater and RO settings does not seem feasible, especially when the off-time of the RO installation for CIP is taken into account. A biweekly CIP of each array is needed at the moment instead of the assumed CIP frequency of once a month. The suggested settings for the current situation are mentioned below:

- Recovery: recovery of 85% is possible without scaling forming on the membranes.
- Flux: lower than 21LMH (can be realized with different membranes or extra skids). Too little research was done to find the optimal flux setting. Testing the lower flux of 18.6LMH gave positive results, however MTC was still not stable when Biox was used as feed source.
- Feedwater source: MBR is preferable above Biox as well when looking at biofouling issues or fouling issues.
- CIP frequency: biweekly CIP of every array
- Cartridge filters: not needed, can be placed for safety reasons but replacement < 2x a year.

An important remark is that this is all based on the pilot results obtained in the research. The component causing the membranes to foul is added as for conditioning of the cooling towers. Conditioning of the cooling towers at Dow will however change in the future. It is not clear if the new chemical will have a better or worse effect on the operation of the RO. The function of the new chemical that will be used is similar to the benzotriazoles, but the molecule is larger and has a higher Mw. As it is designed to be more effective than the benzotriazoles in the presence of a biocide (fed to CT's to minimize microbiological growth) the dosing rate at CT's will be significantly lower (approx 4-5 times) as will be the residual in the blowdown. The classification of the new chemical (ABM toets) is B rather than A for benzotriazoles, which makes a higher potential for biodegradability of the new chemical likely.

4.4.2 Cleaning procedures

Standard cleaning with NaOH and HCl is not sufficient to remove the fouling. The addition of SDS is needed in order to remove the fouling on the RO membranes. It can be considered to CIP multiple arrays together. Following CIP method is suggested:

1. Caustic cleaning with NaOH + SDS:
    a. At pH > 12
    b. At high temperature (preferably 42-45°C)
    c. Add SDS after 2hours of circulation and circulate for 3hours more
2. Acidic cleaning:
    a. At pH < 2.2
    b. Circulation for a long time

A remark is that SDS is available in the pure form (powder) or in a 30% solution (aq). The powder form is not easy to use, so liquid is preferred. However the 30% solution used in the pilot project needs to be stored at temperatures above 21°C, which is above the melting point of 13-21°C.

5. LIST OF MOST USED ABBREVIATIONS

Base Case Scenario – Double layer filtration and biologically activated carbon filter as pretreatment
Biox – effluent from the sweet wastewater treatment plant of Dow, polished with a Dynasand filter
BW- Backwash

CEB – Chemically Enhanced Backwash
CIP – Clean-In-Place

FW- Forward flush
FMEA – Failure Mode & Effects Analysis
Flag Ship Scenario – Constructed wetlands as pretreatment

HSSF CW – Horizontal Sub-Surface Flow Constructed Wetland

IX – Ion Exchange
IX1 – Ion Exchange pilot 1 – production capacity ~ 1 m3/h
IX2 – Ion Exchange pilot 2 – production capacity ~ 6 m3/h

KPI – Key Performance Indicator

MCA - monochloramine
MBR – Membrane BioReactor

OC – Operational Capacity

RO - Reverse Osmosis

SBA – Strong Base Anion
TVC – Total Volume Capacity
TOC – Total Organic Carbon

UF – Ultrafiltration

WAC – Weak Acid Cation
WSSA – Water Supply & Services Agreement

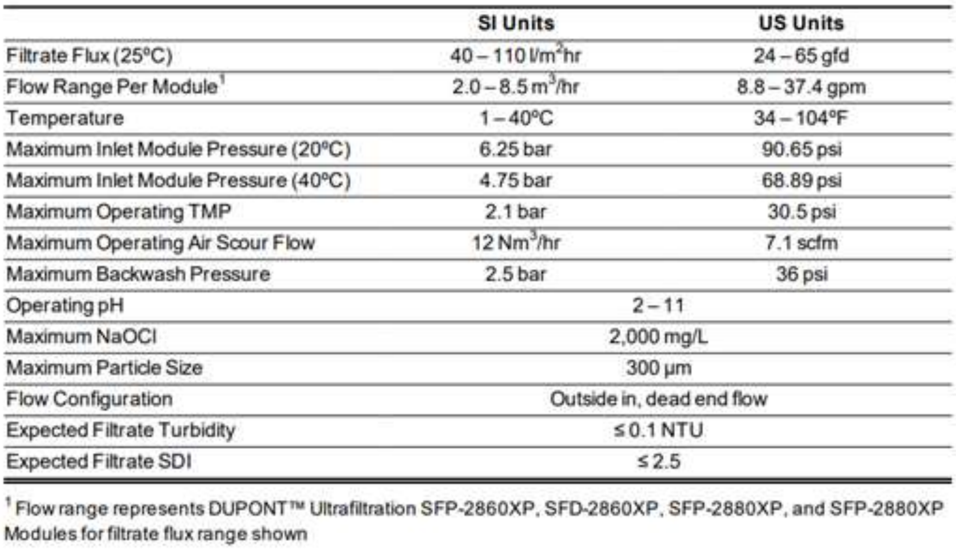
ANNEX A) FEED- AND PRODUCT WATER QUALITY AND QUANTITY

The quality requirements as mentioned in the WSSA.

	Unit	**Feed RWZI-effluent** **TOP-3.9 (avg.-max.)**	**Feed Biox** **TOP-4.2 (avg.-max.)**	**Feed Spuikom** **TOP-3.2 (avg.-max.)**	**Product norm** **TOP-4.1 (avg.-max.)**
Expected flows	**m^3/h**	**280-625**	**430-600**	**50-100**	**430-600**
Na	mg/l	-	-	-	7.7
K	mg/l	-	-	-	1.3
Ca	mg/l	74-84	62-90	102-120	Under detection limit
Mg	mg/l	25-32	-	-	Under detection limit
Mn	mg/l	-	-	0.12-0.4	-
NH_4	mg/l	3.4-9.0	0,4-1,6	1.3-1.6	0.13
Fe	mg/l	-	0.14-0.6	1.0	-
Cl	mg/l	-	136-200	190-250	5.8
F	mg/l	-	-	-	0.1
SO_4	mg/l	120	104-200	120-150	1.5
NO_3	mg/l	27 - 33	8-20	1.2-105	2.9
HCO_3	mg/l	-	-	-	8.2
SiO_2	mg/l	-	-	-	0.16
PO_4-P	mg/l	2-4	0.4-2	0.5-0.7	-
pH	-	8-9	7-8.5	8-9	5.4-6.1
Conductivity @ 25 °C	µS/cm	1500-2750	890-1500	-	40-50
Suspended solids	mg/l	7-10	-	9-20	-
Min. oil	µg/l	100	100	100	-
Chlorophyll-a	µg/l	10-50	-	20-90	-
TOC	mg/l	12-15	25	14-20	-
Legionella	CFU/l	-	3000	-	-
Turbidity	NTU	6-10	0-10	9-20	-

ANNEX B) UF RESEARCH ATTACHMENTS

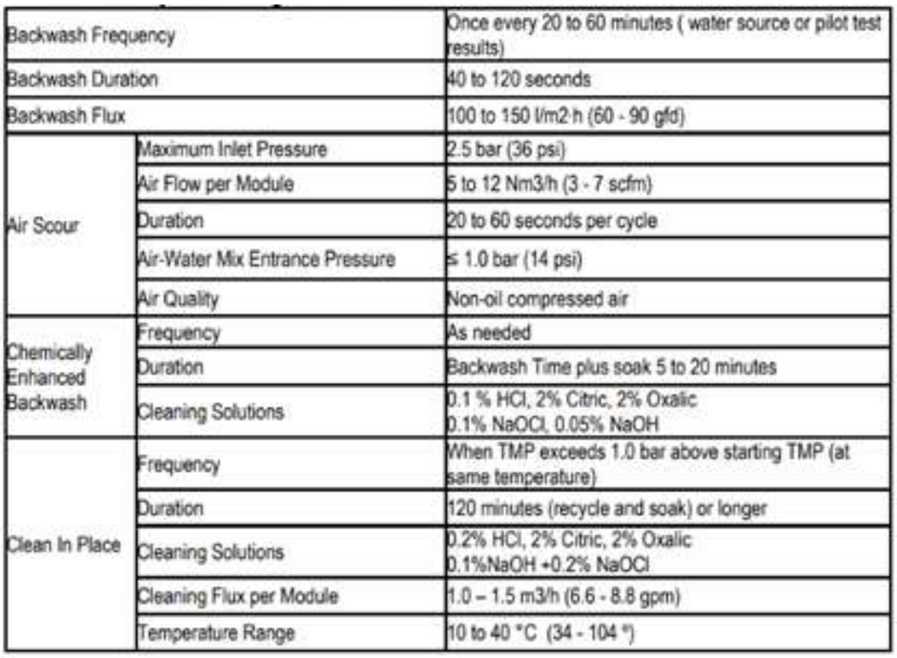
Recommended operating conditions from supplier Dupont for the IntegraFlux™ SFD-2880X modules.



	SI Units	US Units
Filtrate Flux (25°C)	40 – 110 l/m²hr	24 – 65 gfd
Flow Range Per Module[1]	2.0 – 8.5 m³/hr	8.8 – 37.4 gpm
Temperature	1 – 40°C	34 – 104°F
Maximum Inlet Module Pressure (20°C)	6.25 bar	90.65 psi
Maximum Inlet Module Pressure (40°C)	4.75 bar	68.89 psi
Maximum Operating TMP	2.1 bar	30.5 psi
Maximum Operating Air Scour Flow	12 Nm³/hr	7.1 scfm
Maximum Backwash Pressure	2.5 bar	36 psi
Operating pH	2 – 11	
Maximum NaOCl	2,000 mg/L	
Maximum Particle Size	300 µm	
Flow Configuration	Outside in, dead end flow	
Expected Filtrate Turbidity	≤ 0.1 NTU	
Expected Filtrate SDI	≤ 2.5	

[1] Flow range represents DUPONT™ Ultrafiltration SFP-2860XP, SFD-2860XP, SFP-2880XP, and SFP-2880XP Modules for filtrate flux range shown

Recommended cleaning conditions from supplier Dupont for the IntegraFlux™ SFD-2880X modules.



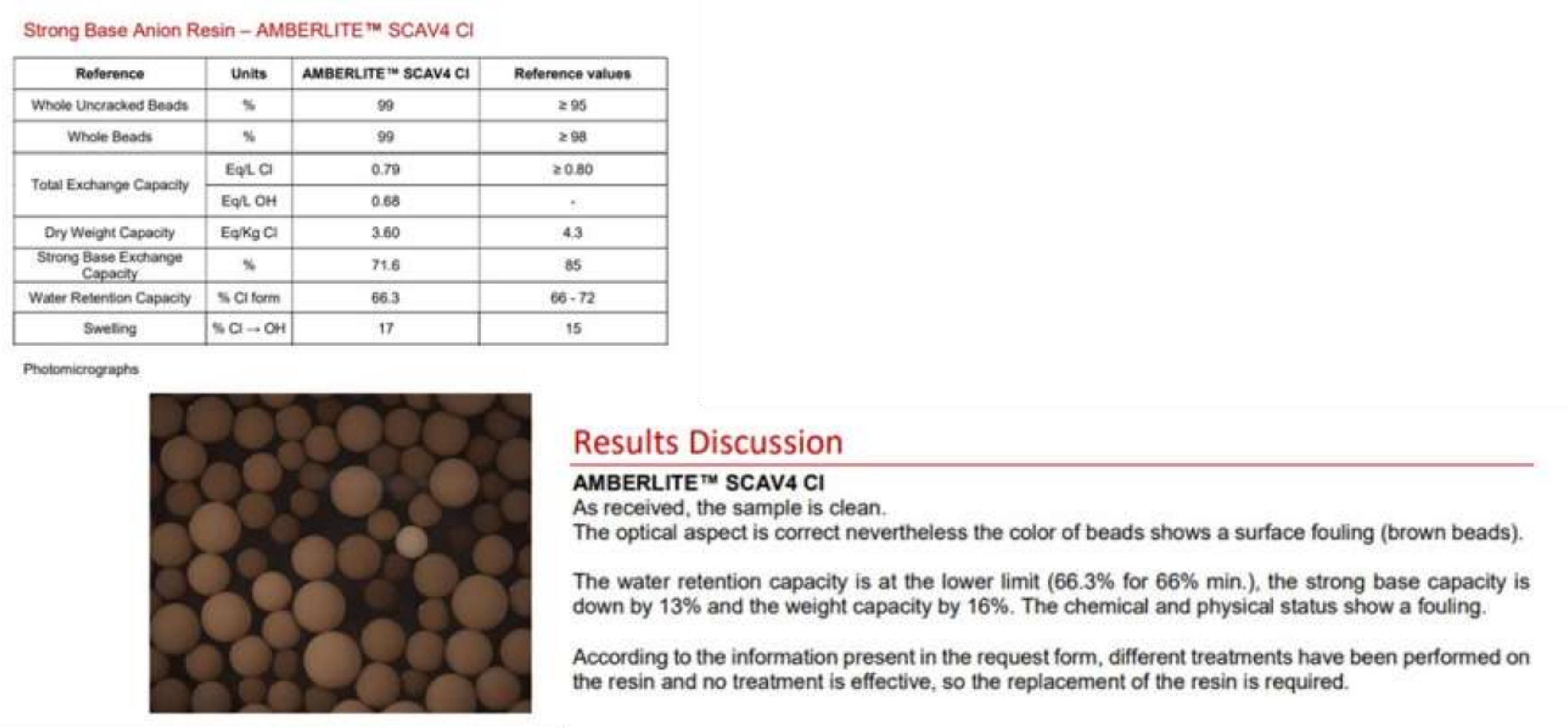
Backwash Frequency		Once every 20 to 60 minutes (water source or pilot test results)
Backwash Duration		40 to 120 seconds
Backwash Flux		100 to 150 l/m2·h (60 - 90 gfd)
Air Scour	Maximum Inlet Pressure	2.5 bar (36 psi)
	Air Flow per Module	5 to 12 Nm3/h (3 - 7 scfm)
	Duration	20 to 60 seconds per cycle
	Air-Water Mix Entrance Pressure	≤ 1.0 bar (14 psi)
	Air Quality	Non-oil compressed air
Chemically Enhanced Backwash	Frequency	As needed
	Duration	Backwash Time plus soak 5 to 20 minutes
	Cleaning Solutions	0.1 % HCl, 2% Citric, 2% Oxalic 0.1% NaOCl, 0.05% NaOH
Clean In Place	Frequency	When TMP exceeds 1.0 bar above starting TMP (at same temperature)
	Duration	120 minutes (recycle and soak) or longer
	Cleaning Solutions	0.2% HCl, 2% Citric, 2% Oxalic 0.1%NaOH +0.2% NaOCl
	Cleaning Flux per Module	1.0 – 1.5 m3/h (6.6 - 8.8 gpm)
	Temperature Range	10 to 40 °C (34 - 104 °)

In the table below, all the tested settings can be found since the start of the research in May 2019.

Period	Water source	Flux	Filtration time	Extra
mei-19	BIOX	80	15	
jun-19	BIOX	80	15	
jun-19	BIOX	80	40	
jul-19	BIOX	90	40	
jul-19	BIOX	80	40	
aug-19	BIOX	90	40	
dec-19	MBR	60	40	
jan-20	MBR	60	40	
jan-20	MBR	80	15	
jan-20	MBR	80	40	
feb-20	MBR	60	15	
feb-20	MBR	80	15	
mrt-20	MBR	60	15	
jun-20	MIX	60	15	
jul-20	MIX	60	15	
aug-20	MIX	60	15	
sep-20	MIX	60	15	
okt-20	CW MIX	60	15	
okt-20	CW MIX	60	40	
okt-20	CW MIX	60	40	NoOX
nov-20	CW BIOX	70	40	
nov-20	CW MIX	60	40	NoOX
nov-20	CW MIX	70	40	
nov-20	CW MIX	70	40	NoOX
dec-20	CW BIOX	65	40	
dec-20	CW MBR	60	60	
dec-20	CW MIX	60	60	
dec-20	CW MIX	65	40	
dec-20	CW MIX	70	40	
jan-21	CW BIOX	60	60	
jan-21	CW MBR	60	60	
jan-21	CW MIX	60	60	
feb-21	CW MIX	60	60	
feb-21	CW MIX	60	60	NoOX
mrt-21	CW BIOX	60	60	BRU
mrt-21	CW MBR	60	60	BRU
mrt-21	CW MIX	60	60	
mrt-21	CW MIX	60	60	BRU
apr-21	CW MIX	60	30	BRU
apr-21	CW MIX	60	60	BRU
apr-21	CW MIX	60	90	BRU

mei-21	CW MIX	60	60	
mei-21	CW MIX	60	60	BRU
mei-21	CW MIX	60	90	BRU
jun-21	CW BIOX	60	120	BRU
jun-21	CW MIX	60	120	BRU
jun-21	CW MIX	60	60	BRU
jul-21	CW BIOX	60	120	BRU
jul-21	CW MBR	60	120	BRU

ANNEX C) SCAV4 RESIN ANALYSES



Strong Base Anion Resin – AMBERLITE™ SCAV4 Cl

Reference	Units	AMBERLITE™ SCAV4 Cl	Reference values
Whole Uncracked Beads	%	99	≥ 95
Whole Beads	%	99	≥ 98
Total Exchange Capacity	Eq/L Cl	0.79	≥ 0.80
	Eq/L OH	0.68	-
Dry Weight Capacity	Eq/Kg Cl	3.60	4.3
Strong Base Exchange Capacity	%	71.6	85
Water Retention Capacity	% Cl form	66.3	66 - 72
Swelling	% Cl → OH	17	15

Photomicrographs

Results Discussion

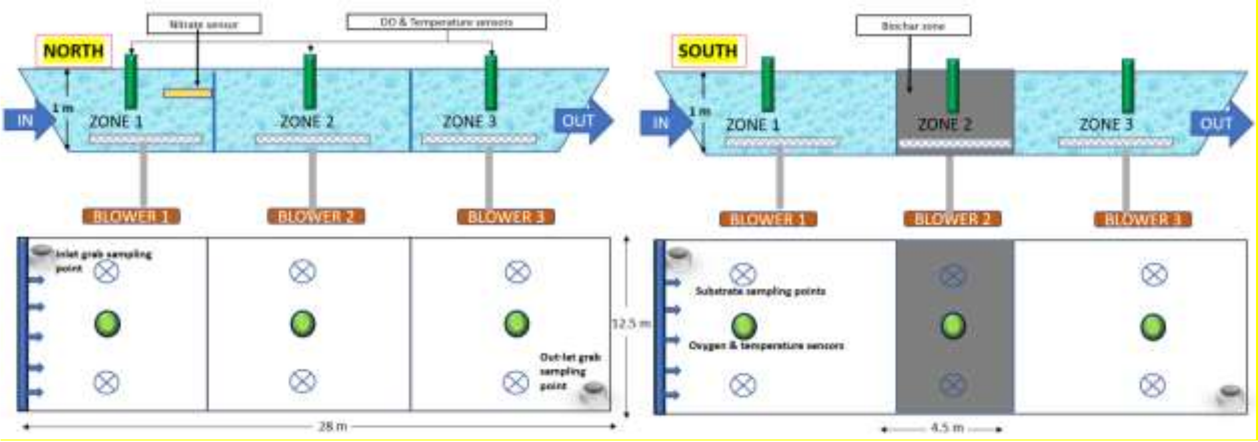
AMBERLITE™ SCAV4 Cl

As received, the sample is clean.
The optical aspect is correct nevertheless the color of beads shows a surface fouling (brown beads).

The water retention capacity is at the lower limit (66.3% for 66% min.), the strong base capacity is down by 13% and the weight capacity by 16%. The chemical and physical status show a fouling.

According to the information present in the request form, different treatments have been performed on the resin and no treatment is effective, so the replacement of the resin is required.

ANNEX D) CONSTRUCTED WETLANDS SCHEMES



ANNEX E) PRELIMINARY DESIGN, ADDENDUM, TSS-MEMO

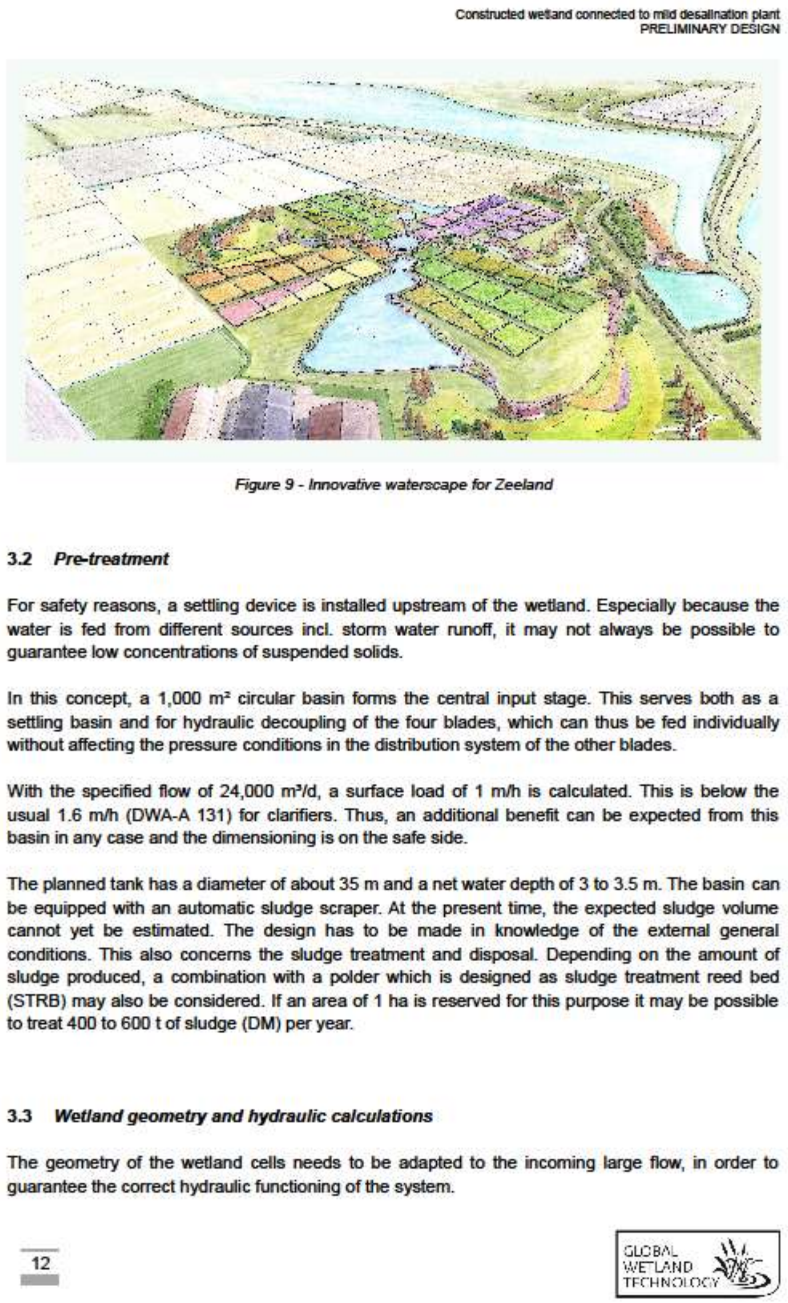


Figure 9 - Innovative waterscape for Zeeland

3.2 *Pre-treatment*

For safety reasons, a settling device is installed upstream of the wetland. Especially because the water is fed from different sources incl. storm water runoff, it may not always be possible to guarantee low concentrations of suspended solids.

In this concept, a 1,000 m² circular basin forms the central input stage. This serves both as a settling basin and for hydraulic decoupling of the four blades, which can thus be fed individually without affecting the pressure conditions in the distribution system of the other blades.

With the specified flow of 24,000 m³/d, a surface load of 1 m/h is calculated. This is below the usual 1.6 m/h (DWA-A 131) for clarifiers. Thus, an additional benefit can be expected from this basin in any case and the dimensioning is on the safe side.

The planned tank has a diameter of about 35 m and a net water depth of 3 to 3.5 m. The basin can be equipped with an automatic sludge scraper. At the present time, the expected sludge volume cannot yet be estimated. The design has to be made in knowledge of the external general conditions. This also concerns the sludge treatment and disposal. Depending on the amount of sludge produced, a combination with a polder which is designed as sludge treatment reed bed (STRB) may also be considered. If an area of 1 ha is reserved for this purpose it may be possible to treat 400 to 600 t of sludge (DM) per year.

3.3 *Wetland geometry and hydraulic calculations*

The geometry of the wetland cells needs to be adapted to the incoming large flow, in order to guarantee the correct hydraulic functioning of the system.

Volgens Rietland BV zou er stabiel gedraaid moeten kunnen worden met een maximale TSS-vracht van 85,5 g/m^2_{inlet}/dag. Binnen de huidige TOP-waarde zou er geen probleem moeten ontstaan. Er zijn twee punten die zorgen baren:

1. In 2020 zijn de TSS-concentraties van effluent van Terneuzen zo hoog, dat dit niet door wetlands behandeld kan worden, er zullen verstoppingen ontstaan.
2. Met de pilot wordt gedraaid op een lage TSS-belasting. Er wordt echter nog steeds verstopping/aangroei waargenomen. Dit is vooral oppervlakkige verstopping door algengroei.

Maatregelen om zuiveringsprestaties full-scale wetland te garanderen

In samenspraak met de projectgroep (bestaande uit Dow, UGent, EIW) is tot consensus gekomen over onderstaande stappen om tot een betrouwbare langdurige werking van het wetland te komen:

1. Extra inlaatoppervlak (is rekening mee gehouden in huidige voorontwerp, ca. 2x pilotontwerp oppervlak).
2. Geen riet planten in eerste 2 meter om doorstroming zo optimaal mogelijk te houden (geen wortels).
3. Eerste 2 meter afdekken om biologische groei op het oppervlak tegen te gaan (bijvoorbeeld wandelpad aanleggen).
4. Ontwerpen van een systematiek om de eerste 2 meter periodiek (5-10 jaar) geheel te vervangen of verschonen.
5. De inlaatzone aan de buitenkant maken. Hierdoor kan men makkelijker met zwaar materiaal de eerste zone afgraven of onderhouden.
6. Beluchting in eerste zone intensiveren. (Dit geeft echter wel een risico op vervuiling van den zone erachter.)

Opmerkingen/risico's

1. Wanneer slibgehaltes zijn zoals in 2020 zal de slibafvoer van zowel Wetland (1x per 5-10 jaar?) als wel MMF in het base case scenario verhogen.
2. Indien er te veel slib of biologische aangroei is, zal het wetland langzaam dichtslibben, met het logische gevolg dat het effect op biologische stabiliteit minder wordt (c.q. lagere verblijftijd). Gezien de pilotresultaten en de aanpassingen op het full-scale ontwerp zou in de slechtste situatie uitgegaan kunnen worden van ca. 0,5 m dichtslibbing per jaar. Het risico is beperkt, omdat men vermindering van prestaties van het wetland ver van tevoren aan kan zien komen (jaren) en daar passende maatregelen op kan nemen (o.a. toplaag verwijderen, grindwasser voor Argex).
3. Door het stoppen van MCA-dosering bij awzi Terneuzen zal er aangroei plaats gaan vinden in de leidingen via Braakman richting DECO en vervolgens in het wetland terecht komen. Risico hiervan wordt gering ingeschat.
4. Realisatie filtratie stap na awzi Terneuzen brengt extra kosten met zich mee in het Flagship scenario. Mogelijk kunnen de MMF filters van DECO worden hergebruikt en worden verplaatst naar Terneuzen. Echter zal gebouw, aanleg leiding materiaal, spoelwater voorziening voor extra kosten zorgen.
5. Operationele kosten zullen aanzienlijk zijn als er periodiek Argex 'gewassen' moet worden.

Base case scenario

Als uitgangspunt voor de belasting van de dubbellaagsfilters (IWZ Dow) met effluent van Terneuzen is genomen:
TSS effluent Terneuzen gem.: 10 mg/l
TSS effluent Terneuzen P90: 20 mg/l

Addendum to:

PRELIMINARY DESIGN

CONSTRUCTED WETLAND CONNECTED TO MILD DESALINATION PLANT

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Date: August 26, 2021