Feasibility study
Feasibility of DOC-laden ion exchange brine treatment at the Andijk III WTW, the Netherlands
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Introduction

The Andijk water treatment works (WTW) of PWN in North Holland has been expanded and upgraded over the years to improve finished water quality, often as an early adopter of breakthrough technologies thus, has been the scene for many innovations.

The first example of this innovation, in 2004, was the replacement of breakpoint chlorination with ultraviolet (UV) light irradiation with peroxide as an advanced oxidation process (AOP) prior to the preexisting downstream biological granular activated carbon (BAC) for primary disinfection and organic contaminant control.

In 2014, the latest example is the pretreatment part of the plant. Originally based on conventional coagulation and rapid sand filtration, this was replaced with an innovative treatment train including suspended ion exchange (SIX®) followed by ceramic membrane filtration. The ceramic microfilter was selected because it provided a more robust filtration barrier, when compared to the conventional sand filter options. To combat fouling of the ceramic membranes during filtration cycles, the SIX® ion exchange process was implemented for its ability to remove the humic substances (HS) as part of the dissolved organic carbon (DOC), which was recognized as a contributor to membrane fouling.

The SIX® process effectively removes approximately 45 to 50 percent of the DOC; however, it produces a DOC-laden brine, which requires disposal and handling. Characteristics of the brine depends on the water source and the SIX© process conditions. The DOC concentration, usually comprised between 0.05 and 0.1 percent, impacts the brine's color. Alongside with the DOC, raw-water inorganic anions also adsorb on the resin and desorb during regeneration, and contribute to the conductivity.

Due to the innovative nature of the SIX© process, the residual brine constitutes a new and unfamiliar type of waste for a water utility; for which standard disposal or treatment routes have not been established yet. Direct discharge of the brine, whenever possible with regards to the composition and the local environment, is the most economical strategy to handle this waste stream. In fact, except for the regenerant (i.e. sodium chloride), all components of the brine originate from the raw water; hence sea water, brackish water or wastewater can serve as receiving bodies as long as discharge limits are respected. Whenever discharge is not possible, several treatment strategies are applicable, from a targeted pretreatment to only remove undesired compounds prior to discharge to the full elimination of the waste stream though zero liquid discharges (ZLD) or in some case zero discharge and resource recovery. In Andijk, a discharge permit through deep well injection has been temporarily granted to discharge the SIX© brine and allow the continuity of water production, under the condition that on the long term treatment solutions are evaluated.

The presence of DOC in the SIX© brine could potentially hamper the efficiency and long term operability of the processes.

To provide long term treatment solutions for PWN, and utilities opting for ion exchange treatments to improve DOC removal from their drinking water production, different possible treatment pathways have been tested for the treatment of the DOC-laden ion exchange brine produced in Andijk as part of the DOC2Cs project. Results of the feasibility tests are summarized in this report.

Background

This section provides some background information about the Andijk III water source, water quality, and treatment processes.

Description of source waters

The water supply to the Andijk III WTW is from IJsselmeer, or Lake IJssel. It is a shallow, man-made reservoir which is primarily fed by the Rhine River. There is a small, inner reservoir which holds about three days of water supply at the inlet location to the water plant. This small reservoir is hydraulically connected to Lake IJssel; however this connection can be closed in the event of a water quality incident (e.g., spike of a pesticide or industrial discharge chemical concentration). This reservoir also allows for some pre-settling of suspended solids.

Historical development of Andijk WTW

Andijk WTW was originally inaugurated in 1968 as a conventional surface water treatment plant based on breakpoint chlorination and coagulation sedimentation and filtration (CSF). The plant was first improved in 1978 with the addition of granulated activated carbon (GAC) to reduce residual taste and odor compounds. The next major improvement of the plant occurred in 2004, when operations of breakpoint chlorination was replaced with an advanced oxidation post-treatment based on Medium Pressure UV/H_2O_2 prior to the existing GAC. This retrofit was motivated by increasingly tight regulations of Trihalomethanes (THM) at the time, the requirement for further disinfection capacity and for a universal barrier against organic micropollutants [1]. When after 40 years of operation the time to replace the conventional pre-treatment came, capacity of the plant needed to be increased; in addition the desire was to increase DOC removal and UV transmission (UVT) to increase the efficiency of the AOP and provide an absolute barrier to suspended solids and colloidal matter. Results of a vast research program promoted the use of ion exchange followed by ceramic microfiltration, which led to the development of the SIX© and the Ceramac© to specifically address the requirements at Andijk WTW.

Description of treatment processes at Andijk III WTW

In May 2014, the new pre-treatment based on SIX© and Ceramac© was put into operation. The full treatment train, named Andijk III, is shown in Figure 1. First, sodium hydroxide (NaOH) is added to the water prior to storage in the reservoir. Then carbon dioxide (CO_2) is added before the water is screened (200 micron). Next, the water enters the SIX® process, where anion exchange resin is dosed primarily for the removal of DOC. The resin is then separated from the water and immediately regenerated with a sodium chloride solution. Hydrogen peroxide (H_2O_2) for the post treatment is dosed upstream of the CeraMac® microfiltration ceramic membrane filtration process to also reduce fouling. To clean the membranes, a low pH solution of H_2O_2 is used in some enhanced backwashes and a chlorine solution is used for other enhanced backwashes. Water then travels to the ultraviolet (UV) irradiation process, which performs as an advanced oxidation process (AOP) due to there being a H_2O_2 residual before entering the UV reactors. The water then passes through biologically active carbon (BAC) at a contact time of about 15 minutes before being dosed with a low concentration of chlorine dioxide (ClO_2) and then screened. Water is then sent to distribution.

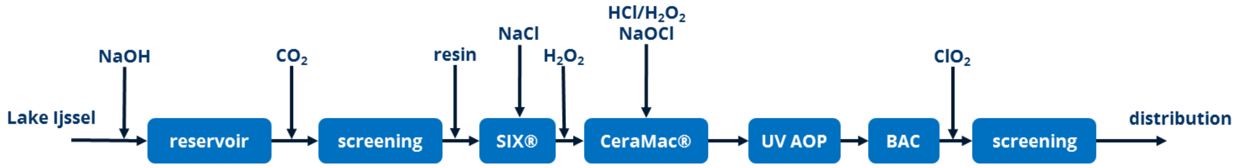

Figure 1:Process flow diagram of the Andijk III water treatment plant

<u>Description of the SIX© process operation and resin regeneration</u>

For DOC removal from surface water in Andijk III, 12 mg/L of resin (Lewatit S5128) is continuously dosed in the SIX© influent water and flows through the contactor in single pass. The residence time for the water and the resin is 30 minutes, at the end of which, the resin is separated by lamellas and collected for regeneration.

The influent and effluent averages qualities and removal percentages of the SIX© are summarized in table 1. Next to the targeted DOC, some inorganic anions present in the influent water such as sulphate, bicarbonate and nitrate are also retained. On one hand, this untargeted adoption of inorganic anions has a positive impact on the corrosion index in the distribution system, but on the other hand, it results in a higher release of chloride in effluent water and higher consumption of NaCl during regeneration. The two effects should therefore be balanced during optimization of the SIX©.

Table 1: Performance of the SIX© process in operation in Andijk

	Cl^-	Na^+	HCO_3^-	SO_4^{2-}	NO_3^-	DOC
SIX© influent (mg/l)	140 ± 30	100 ± 40	135 ± 20	55 ± 10	4,5 ± 4	5 ± 1
SIX© effluent (mg/l)	190 ± 50	100 ± 40	110 ± 15	12 ±8	4 ± 3	2,5 ± 1
removal (%)	-	-	20%	78%	11%	50%

DOC is here used as the generic parameters for the removal of organic matter. Alternatively, the use of the chromatographic analytical technique known as the liquid chromatography – organic carbon detection (LC-OCD) allows to further distinguish the following fractions of organic matter between Biopolymers (BP), Humic Substances (HS), Building Blocks (BB), Low Molecular Weight Acids (LMWA) and Low Molecular Weight Neutrals (LMWN). In LC-OCD, the different fractions are characterized mainly on the basis of molecular size, although multiple factors (hydrophobicity, inorganic interactions, ionic strength, pH) also have influence. With this tool, the specificity of the ion exchange resin for the removal of the humic substances fraction could be established as detailed in table 2.

Table 2: Further characterization of DOC removal performance of the SIX© process in Andijk

	DOC	BP	HS	BB	LMWA	LMWN
SIX© influent (mg/l)	5 ± 1	780 ± 500	2800 ± 1000	880 ± 150	760 ± 150	0 ± 0
SIX© effluent (mg/l)	2,5 ± 1	700 ± 500	850 ± 400	500 ± 100	480 ±50	0 ± 0
removal (%)	50%	10%	82%	43%	36%	-

The regeneration, operated in batch every 30 minutes, consists of contacting the NOM-loaded resin with a sodium chloride solution to force the desorption of NOM and other adsorbed anions (e.g., sulfate and nitrate) and the replacement of chloride ions on the resin surface. Optimization of the process has led to the reuse of the sodium chloride solution to minimize its consumption. In fact, different brine solutions are used consecutively, starting with a four times used solution, followed by fresher solutions until freshly made up brine is applied. Then the regenerated resin is rinsed with water. After being used for the fifth time, the spent brine is discarded as the final waste. The SIX© process generates a brine volume of approximately 0,6% of the water production. In Andijk, this is equivalent to 30 m^3/h of brine at maximum capacity.

Description of SIX© waste brine

The average composition and main parameters associated with the SIX© brine are given in table 3, with a variation between minimum and maximum. The variation in composition depends on: 1) the composition of the Lake IJssel water, which varies with the season or due to climate events; and 2) the performance of the SIX© process, especially the adsorption and desorption capacity of the resin and the NaCl use. The residual water in the regeneration vessel and pipes also induces a significant dilution factor. The relatively high resin dose and the use of resin in single pass lead the SIX© process to produce a waste brine with typically lower concentrations of organic and inorganic ions than usually seen in ion exchange.

Table 3: typical composition of the SIX© brine in Andijk

parameter	unit	min	average	max
Chloride	g/l Cl^-	2	4	7
Sodium	g/l Na^+	3	7	10
Bicarbonate	g/l HCO_3^-	1	3	5
Sulphate	g/l SO_4^{2-}	3	6	10
Nitrate	mg/l NO_3^-	1.2	26	120
DOC	mg/l C	150	270	550
Conductivity	mS/m	850	2070	2930
pH		8.5	8.8	9.1
Suspended solids	mg/l	0.3	2.3	14.6
Total hardness	mmol/l	0.76	1.15	1.61

The specific fractions of DOC present in the SIX© brine was also investigated with LC-OCD. The results from November 2017 to September 2019, illustrated in figure 2, confirmed the preponderance of the humic substances in the DOC due to the selectivity of the ion exchange resin. Despite a large (±112%) variation in total DOC concentration in the brine over time, the relative fractionation of the DOC remains stable with 0.6% (±0.3) of BP, 78% (±3.1) of HS, 14% (±1.9) of BB and 7% (±0.5) of LMWA and LMWN.

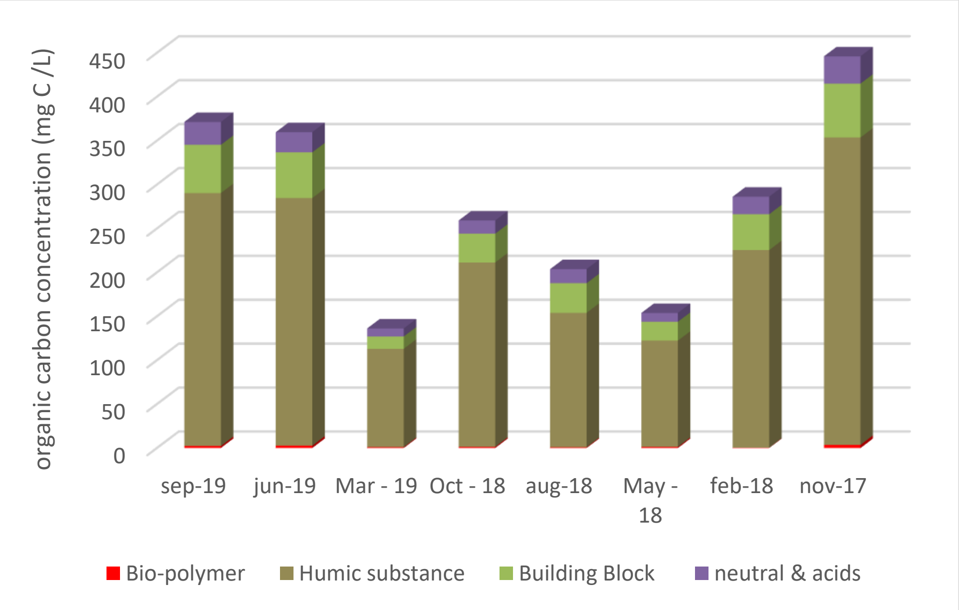

Figure 2: LC-OCD analysis of the DOC in the brine over time

A well-known characteristic of humic substances is their structural complexity involving aromatic blocks and alkyl chains with a diversity of charged functional groups. Consequently, they form complexes which increase mobility of heavy metals and possibly other micro-pollutants throughout the treatment and cause fouling in membrane processes. As part of the humic substances, the humic acids have a molecular weight between 1500 and 50000 Da and the fulvic acids between 600 and 1000 Da. Both species are soluble in water and rather recalcitrant to biological degradation.

Brine treatment strategies and technologies considered

This section lists the possible treatment strategies for the SIX© brine and discusses the ones applicable to Andijk III. After what the relevant treatment technologies to achieve the treatment strategies are described.

General treatment strategies for the SIX© brine

Whenever there is an opportunity locally and the conditions for environmental preservation are met, the direct discharge of the SIX© brine, usually after dilution, would still constitute the simplest and most economical way to dispose of it. In addition, compared to the current treatment technologies, discharge can be the option with the lowest environmental impact (i.e., when considering energy, CO_2 emission, resources and chemicals used). Examples of suitable discharge options include, but are not limited to, a brackish aquifer, a waste water treatment plant or the sea; some of which are largely regulated and generally require a permit. If the option is not available however, treatment of the brine becomes a necessity which can be considered as part of three main strategies:

1- Pretreatment: A pre-treatment strategy can be put in place when one or more specific components or parameters of the brine restrain its ability to be discharged. Examples include an excess of sulfate ions posing a risk of corrosion in the pipes to the WWTP, a specific parameter inadequate with the receiving water body such as the presence of color when considering discharge in the sea, or again a source of toxicity such as micro-pollutants. In such cases, the treatment strategy will be directed to the reduction of the troublesome component to meet the discharge requirements.

2- Volume Reduction: In case of a lack of discharge options in the surrounding area of the treatment plant and the waste brine requires transportation off site to an environmental service provider. In this case, it might be advantageous to reduce the volume of spent brine with high recovery or apply zero liquid discharge (ZLD) types of treatments. High recovery refers to the extraction of typically over 90 percent of the volume of water, which is often recycled or reused, while ZLD implies that the wastes are only generated in a solid form.
3- Separation and Recovery for Secondary Reuse: Finally, treatment can be employed for the separation and recovery of the different salts or organics to reuse them as secondary products. If all compounds of the spent brine find a reuse application, the process is qualified as a zero discharge solution. The recovery of a pure form of sodium chloride is usually desirable with ion exchange processes, despite its low market value, so that can be reused onsite in the next cycle of resin regeneration, thus reducing the chemical demand on the ion exchange process [2]. Another specific secondary product of ion exchange treatment is the DOC. Due to the selectivity of the resin, humic and fulvic acids fractions constitute the majority of the DOC in the brine which, when purified, can be used in the agricultural industry and has a relatively high market value. The beneficial reuse of humic substances from anion exchange spent brine as feed additive and crops enhancer is currently under investigation at PWNT and De Watergroep, partners in the DOC2C's project.

Brine treatment strategies and technology selection process in Andijk III
In Andijk, the direct discharge through deep well infiltration has always been considered a temporary solution granted by the environmental authorities to assure the continuity of water production while durable solutions were investigated. Two implementable alternative solutions have been considered in this report :

- Zero liquid discharge would be the necessary option if no discharge permit were granted anymore. Several membrane and evaporative technologies were investigated for the purpose of reducing volume of the SIX© brine to crystallization. Pretreatment technologies for the removal of DOC prior to membrane treatment are also considered.
- Discharge to Lake IJssel after extraction, recovery and reuse of the NaCl, which would only be possible with a permit from the environmental authority. This option also gives the opportunity for long term development, to add a treatment step for the extraction and reuse of the DOC as a valued secondary product. This is currently under research.

The feasibility two option was assessed technically and financially in the rest of this report.

Table 4: treatment technologies for brines and waste waters

Technology	Strategy/ purpose	Prospects and risks when applied to SIX© brine
Volume reduction / water recovery		
RO	First step in ZLD to concentrate the brine up to 80g/L TDS	Well established and widely available technology. Organic fouling due to the HS is foreseen as the main risk and will require pre-treatment or mitigation tool.
Evaporation	Final step in ZLD comprising crystallization.	Several processes using commercially available technologies with various heat transfer methods. Energy efficiency is to be investigated
NaCl recovery		

Nanofiltration	Separation of NaCl and reduction of brine volume	Economical treatment. Permeate requires treatment with conventional RO prior to reuse. Risk of fouling.
Electrodialysis	Separation and concentration of NaCl / partial demineralization of the brine	Monovalent selective membranes for direct reuse of the concentrate in the SIX©.
DOC removal / color elimination		
Coagulation	DOC removal	Low investment – production of sludge and high chemical demand. However HS don't coagulate efficiently.
Adsorption / Oxidation	DOC and color removal	The presence of bicarbonate in the brine may reduce the process efficiency.

Several treatment processes seen in literature have not been assessed in this feasibility study because either they are not widely applied and available at the moment or because the opportunity for tests have not presented themselves. For example:

- Forward osmosis which could potentially be applicable for volume reduction as a first step in ZLD but would require a conventional RO to recover the draw solution. This technology has been applied to treat industrial wastewater with a high fouling risks.
- Membrane distillation also theoretically provides a volume reduction step with lower risk of fouling as a first step in ZLD
- Eutectic freeze crystallization is an alternative to evaporative crystallizers to achieve the ZLD. The technology operates at a temperature meeting the eutectic conditions of a brine, defined on a binary phase diagram as the point of equilibrium between ice, salt and solution. Upon cooling a system at the eutectic concentration, the two solids will simultaneously crystallize.
- Electrocoagulation, is a non-chemical means of coagulation applicable for the removal of DOC in which an electrical current is applied between two electrodes causing the electrolytic oxidation of the electrode material and generating coagulate species in situ.

Technology description

Pressure driven membrane systems (nanofiltration / reverse osmosis)
A membrane constitutes thin films of synthetic organic or inorganic material to operate a selective separation between the components in brine under the effect of hydraulic pressure. Membrane treatments lead to the production of two streams, a permeate which contains water and the specific ions that are able to pass through the membrane, and a concentrate, where retained ions are kept in a reduced volume of water. Different size cut-offs of membranes available allow the retention of different compounds; microfiltration (MF) for the retention of suspended solids, ultrafiltration (UF) for macromolecules, nanofiltration (NF) for the dissolved multivalent and organic ions and reverse osmosis (RO) for all ionic compounds (Ahmadun et al., 2009).

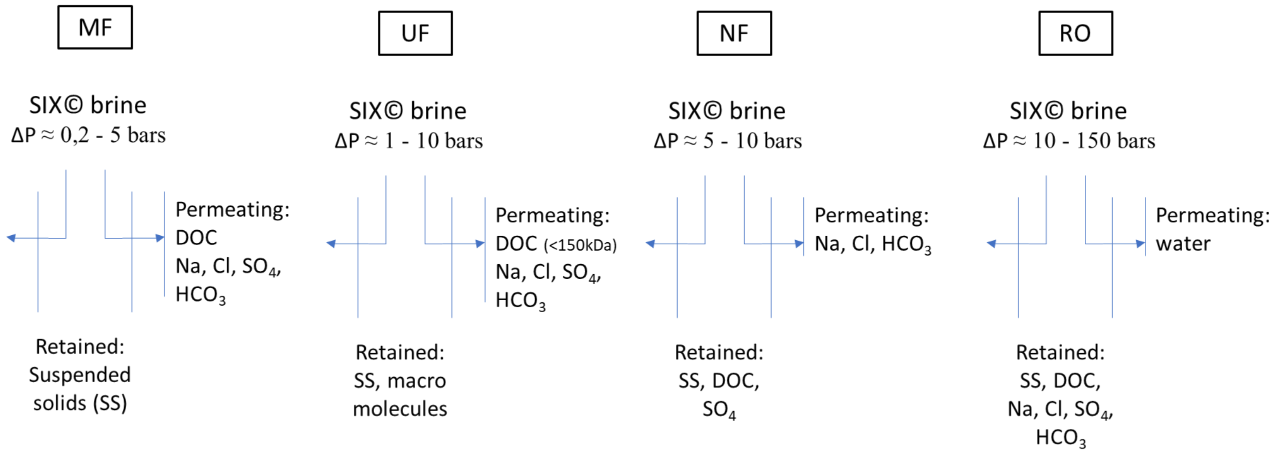

Figure 3: schematic of the different membrane's cut off

RO is commonly employed to recycle water from industrial waste streams and brines and to reduce volumes up to near scaling limits. Treating ion exchange brines specifically, NF is equally applicable as the permeate containing sodium chloride can be reused as the supplemental "make-up" regenerant solution for the ion exchange resin.

Membrane process are usually considered cost competitive in comparison to other treatment processes; they are therefore widely applied and available in various configurations and material. The standard applications include spiral wound or capillary elements kept in pressure vessels. To combat fouling frequently occurring on the membranes several strategies are put in place. One consists in amending the process to create turbulent flow at the surface of the membrane and disturb the formation of a cake layer. Another possible strategy is to apply pre-treatment to remove the fouling material from the brine ahead of the membranes. A last strategy is to improve the cleanability of the membrane using ceramic material well able to sustain harsh chemical conditions. Currently ceramic MF and UF are commercially available, and research efforts are put towards reducing the pore size of ceramic membranes to reach NF.

As part of the DOC2C's project, several configurations of pressure driven membranes were assessed to treat the SIX© brine. A standard NF element was run in a pilot with a high velocity recirculation loop for volume reduction and NaCl recovery. A ceramic NF element was assessed on laboratory scale. Ultra-high pressure RO was assessed with an extended pre-treatment of coagulation and ceramic MF as a first step to a ZLD. And an innovative process using vibratory shears to improve RO filtration called vibratory shear enhanced processing (VSEP) was also considered as a first step to ZLD.

Vibratory shear enhanced processing (VSEP)

In vibratory shear enhanced processing (VSEP), membranes are configured on flat disks assembled in a pack submitted to continuous vibrations. The ultimate goal of this specific design is to prevent the deposition of particles and the formation of cake layer at the surface of the membrane to improve the flux and reduce fouling.

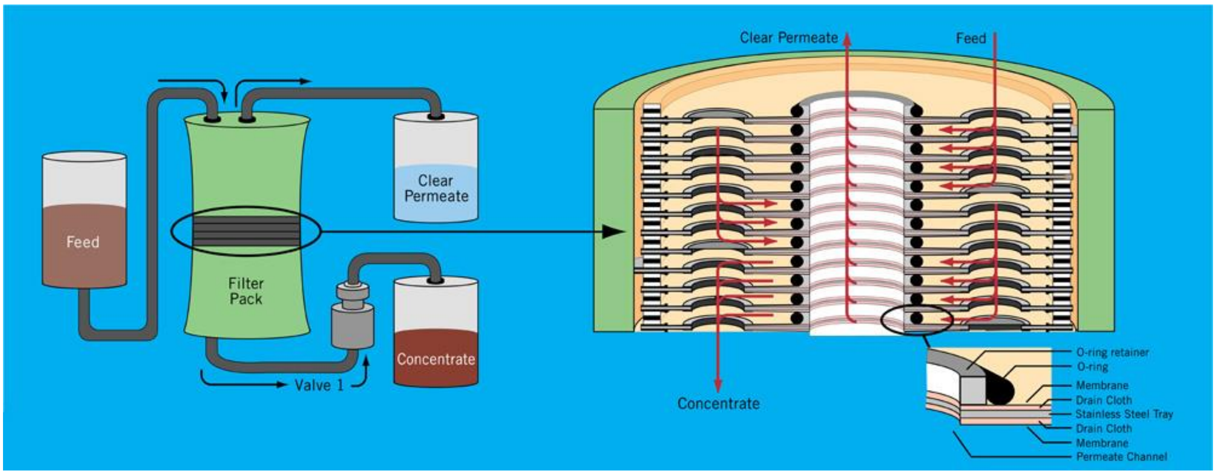

Figure 4: schematic of the VSEP process (ref: https://www.vsep.com/technology/)

A standard VSEP membrane pack contains 300 supporting discs with flat RO membrane sheets disposed on both sides. The system runs in single pass system at fixed pressure (up to 68 bars). During operation, the brine to be concentrated is distributed homogenously between the discs; at the membrane surface a gentle cross flow is applied slowly moving undissolved material towards the concentrate channel, while the permeate is collected at the center (figure 4). Undissolved material and gel layer are prevented from settling on the membrane through shearing action induced by the torsion oscillation of the pack. These vibrations occur continuously during operation and CIP (cleaning in place). The amplitude is optimizable to the application and flow rate requirement in a range of 1.9 to 3.2cm peak to peak; the frequency is approximately 53Hz.

Electrodialysis

Electrodialysis involves the separation of ions through a semipermeable membrane exploiting the fact that ions move across these membranes when a direct current is applied. Electrodialysis cells are set up so that alternating anion exchange membranes (AEMs) and cation exchange membranes (CEMs) sit between two electrodes forming parallel solution channels. When a solution containing a mixture of anions and cations is passed through these channels anions migrate through the AEMs and cations through the CEMs. This causes an increase in ion concentration in alternating channels, known as the concentrate, and a decrease in ion concentration in the other channels known as the diluate. The deposition of an extra layer of monovalent selective polymers on the surface of the membrane permits the specific recovery of monovalent ions such as sodium and chloride.

Applied to the treatment of the SIX© brine with monovalent selective membranes, the movement of sodium, chloride and, to a lesser extent bicarbonate to the concentrate allows their recovery at the desired concentration for the regeneration of the ion exchange resin. The treated SIX© brine, or diluate, on the other hand, is almost fully depleted of the chloride and large parts of the sodium. The remaining organic and inorganic ions mostly originate from the source and could be returned with an appropriated dilution ratio or disposed in any available discharge site with a reduced conductivity.

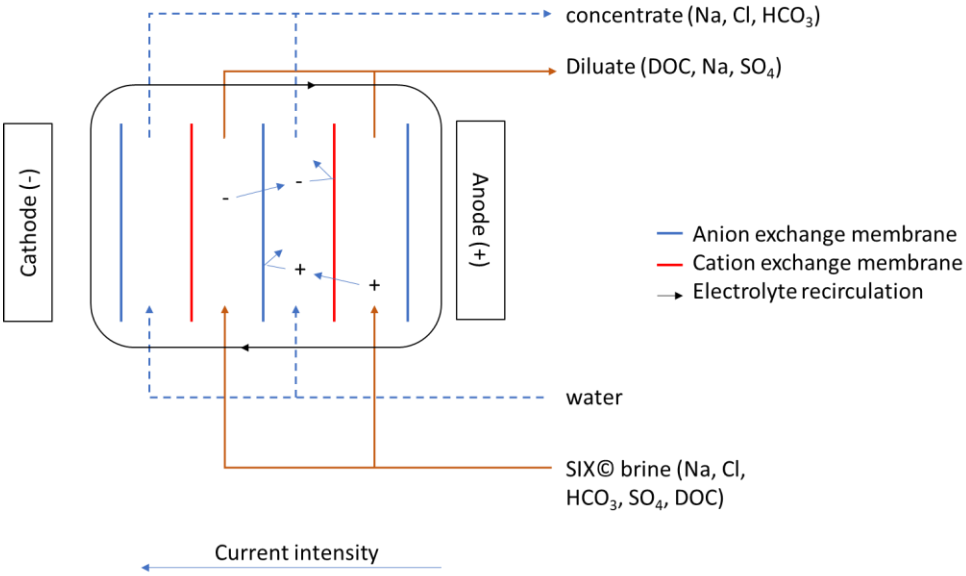

Figure 5: Electrodialysis principle with monovalent selective membranes

Evaporative thermal systems

Thermal systems exploit the change of the state of water at a threshold temperature and pressure to separate it from the brine and achieve volume reduction, concentration of the dissolved solids and when solubility levels are surpassed, crystallization of the salts. During evaporation, the pressure and temperature of the brine are brought to or just below the boiling point of the liquid so that water can escape as vapor. Traditionally, separated crystallizers handle the salt precipitation in a separate step, although some advantage can be found in combining the two steps. Several configurations of industrial evaporators and crystallizers exist which differ from one another with regard to the methods of evaporation and heat transfer. Commercial systems use a combination of a type of evaporator (ie: falling film, forced recirculation, submerged tube, etc.), the energy supply (steam/power) and energy saving (described in figure 6).

Multi-stage flash distillation and multiple-effect distillation are the most recognized and leading evaporation processes used in seawater and brackish water desalination. The multiple effect consists in reusing the vapor produced from one effect as the heat source for another. Consequently, evaporation in the next effect must occur at a lower temperature thus the vacuum is increased to maintain the system at its boiling point. This way only the first effect requires an external source of steam to ensure a sustainable use of thermal energy. However, the current designs and construction materials of multiple-effect evaporators are not adapted for the treatment of brines with as high TDS as the SIX© brine [3]. Instead, industrial evaporation processes commonly used for the treatment of brine can be based on:

Atmospheric evaporator:

The atmospheric evaporator is one of the simplest designs available in which an air stream is pushed through the brine to strip the water as vapor and vent it to the atmosphere. A continuous source of heat is required to warm either the air stream, the brine, or both. Due to the low instrumentation required, the atmospheric evaporator is considered robust, however it is not energy efficient. Therefore this configuration is mostly used when excess of waste heat is available at the plant.

Humidification / dehumidification (HDH)
HDH relies on the ability of air to carry water vapor at elevated temperatures and atmospheric pressure. In an adjacent chamber, the humid air dehumidifies by precipitation in contact with a cold surface. The waste heat from condensing water can be re-used for pre-heating the inlet brine. This system was developed to simplify the complex mechanical designs of conventional evaporators.

Mechanical vapor recompression (MVR)
MVR refers to energy recovery processes used during evaporation: after low-pressure water vapor is created under vacuum, a compressor is used to reduce the volume of gas until condensation which results in a gain of energy by the water in the form of a temperature rise. This energy is then reintroduced in the recirculating brine and feed brine by heat exchangers to keep the temperature at boiling point without external energy inputs. This configuration is therefore possible with electrical power as a single source of energy.

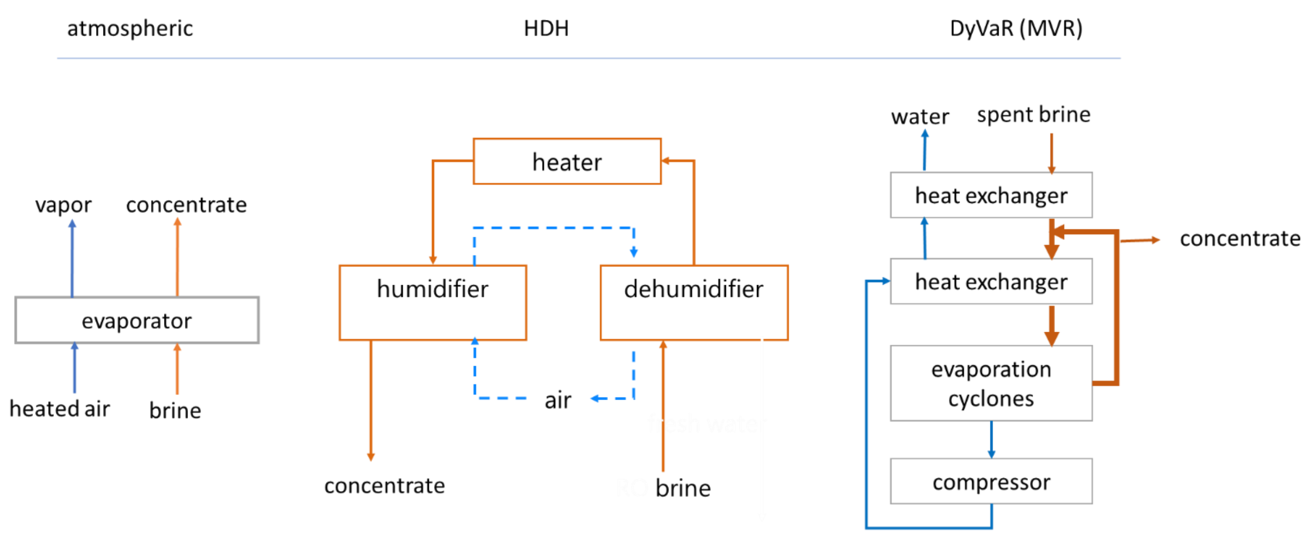

Figure 6: representation of the evaporation processes applicable to SIX© brine

During the DOC2C's project, the treatability of the SIX© brine to cyclization and zero liquid discharge was investigated on a pilot scale Dynamic Vapor Recompression (DyVaR) unit, based on the principle of MVR because thermal energy was not available onsite in Andijk. The energy requirements for other thermal systems were evaluated based on model calculations by the technology providers.

The DyVaR process works on the principles of forced liquid recirculation and vapor recompression. The SIX© brine first enters a pre-heating step, to reach near process temperatures by contact with recovered heat from the exiting condensate. After that the pre-heated raw brine enters the recirculation stream. There a continuous flow of brine circulates through the main heat exchanger, and picks up heat from the condensing water vapor, then through the evaporation cyclones. When entering the evaporation cyclones, the brine is forced into a water layer on the wall of the unit so that the evaporating water can be collected from the middle. A compressor creates a vacuum inside the unit which reduces the boiling point of the salinizing solution and extracts the evaporated water. Only a portion of the water is evaporated during a cycle, the remaining brine is pushed into the suction side of the recirculation pump to go through the same process again. This way the concentration of the recirculated brine gradually increases until it gets to its desired concentration and/or starts to crystallize and form solids. This can be regulated by discharging brine directly from the recirculation stream. The water vapor that is extracted with the compressor is compressed which increases its pressure and temperature. Because of the increase in pressure and temperature the water vapor can be used to provide heat to the recirculated brine by condensing back to a liquid. The condensate flows through the pre-heater where it gives off its remaining heat to the raw water coming into the process and exits as fresh water.

Enhanced chemical coagulation
Coagulation is the chemical process of creating and growing (flocculation) aggregates by adding metallic salts as a coagulant. The positive charge of the metal coagulant provokes the destabilization of colloids in the water by neutralization of their charges. Once the zeta potential at the surface of the colloids is close to zero, they will conglomerate into micro flocs and grow into flocs which can be separated from the water.

Coagulation has become the standard method in drinking water treatment for the removal of suspended solids and colloids. By adjusting pH, coagulation also has the ability to remove parts of the DOC; it is then referred to as enhanced coagulation. The main mechanism involved is the adsorption of DOC onto the hydroxide flocs formed during coagulation. In addition, it is admitted that not all fractions of DOC will coagulate, mostly the non-polar and non-ionized. Adjusting the pH during enhanced coagulation therefore aims at neutralizing the HA to increase their removal.

Carbon material adsorption – electrochemical regeneration
Activated carbon is an efficient adsorbents of DOC, however it is limited in treatment capacity by the requirement for reactivation, usually performed off site, after its adsorption capacity is exhausted. Treating SIX© brine would be considered inapplicable due to its high DOC content and the frequency of regeneration that would be required. To overcome this main limitation, adsorption processes combined with in situ electrochemical regeneration have been developed.

The principle of electrochemical regeneration relies on the application of an electrical current across the exhausted bed of polarized carbon based material, causing 1) the desorption and 2) the anodic oxidation of the DOC [4]. The desorption occurs through two main mechanisms:

- The changes in pH due to the formation of acidic protons (H^+) by oxidation at the anode and basic hydroxyl ions (OH^-) by reduction reactions at the cathode. These acidic and basic fronts are usually sufficient to disturb the adsorptive equilibria of DOC on the carbon adsorbent and cause desorption.
- Electro-desorption; under an electrical current the polarized carbon adsorbent behaves as a semiconductor with the surface charge of its electrode and forms electrical bonds with the charged adsorbate. Upon removal of the current, the adsorbate will be released in solution.

The simultaneous oxidation and mineralization of the released organic is essential to the efficiency of the process to avoid the subsequent re-adsorption. Direct and indirect oxidation occur simultaneously during the process as part of the three main destruction mechanisms:

- Direct oxidation occurs via the transfer of electrons at the surface of the anode to the adsorbed DOC.
- Indirect anodic oxidation occurs via the production of hydroxyl radicals and other oxidizing species, i.e.: chlorine species ($HOCl$, ^-OCl, Cl_2) through reduction reactions at the anode. The oxidizing agents, especially the hydroxyl radicals will in turn degrade the DOC until full mineralization through dehydrogenation (abstraction of H^+), hydroxylation (addition to a unsaturated bond) or electron transfer.

- Indirect cathodic oxidation via the production hydrogen peroxides at the cathode. The addition of a metal catalyst such as Fe(II) can promote the Fenton reaction and the production of hydroxyl radicals which is a more powerful oxidizing agent.

As part of the DOC2C's project, the organic destruction cell™ (ODC), developed by Arvia Technologies and operating on a similar principle as described here, was assessed for the removal of DOC and color in the SIX© brine.

Organic destruction cell™ (ODC)
The OCD process was developed by combining the adsorption of DOC onto a graphite bi-sulphate intercalation adsorbent called Nyex™ and the simultaneous regeneration of this media with anodic oxidation[5]. Particularities of the Nyex™ include the high conductivity and the non-porous surface. Two models of the technology are available:

- The Nyex™-a treatment process focusses on the adsorption and electrochemical regeneration at low current density to mineralize the DOC adsorbed on the surface of the Nyex into H_2O, H_2 and CO_2.
- And the Nyex™-e treatment process which operates at higher current density in order to stimulate the formation of hydroxyl radicals and degrade the unabsorbed DOC through indirect oxidation.

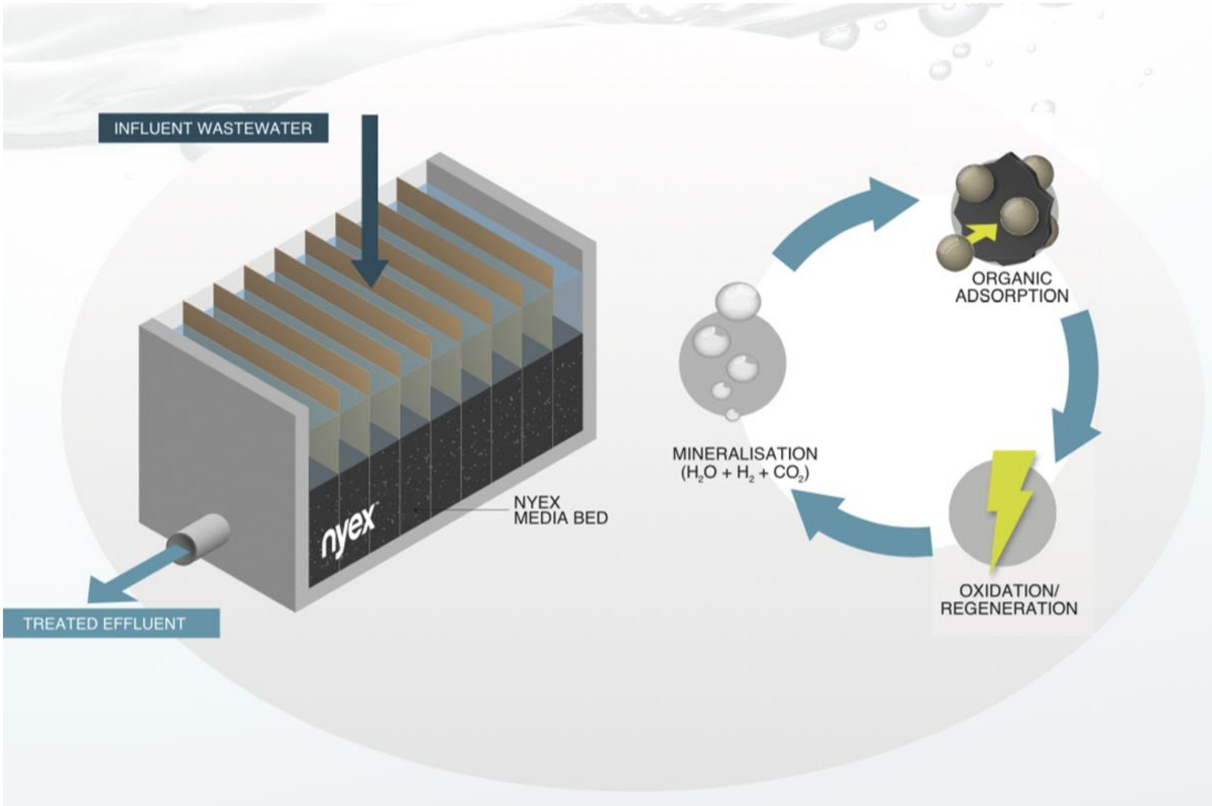

Figure 7: schematic of the ODC process (ref: http://iberospec.com/?portfolio=arvia)

Technical feasibility

In this section, technologies described earlier have been assessed independently on the SIX© brine. The short term evaluations performed on pilot scale provides information about the performance of the process in terms of separation properties, removal percentages, etc.; and allows to assess the quality of the effluents. The long term continuous evaluations bring in additional information about optimization of the process, long term operability and design parameters. In the last subsections, the technical feasibility of the two treatment strategies, ZLD and NaCl reuse, are summarized with the findings of the technology evaluations.

<u>Continuous pilot evaluation of NaCl recovery</u>

Nanofiltration

The nanofiltration was investigated in an early stage of the development of the SIX© process with a double objective to reduce the volume of SIX© brine to dispose of and to recover part of the sodium chloride through the permeate for reuse. At the time of investigation a biological denitrification pilot was operating upfront which was later abandoned after optimization of salt use on the SIX© process.

Specific goals for this pilot study were:

1- Define the separation properties of the membrane between concentrate and permeate.
2- Define the operational parameters: recovery, applied pressure, membrane transport coefficient.
3- Define the long term operability and effect of the brine composition on membrane fouling.

Material and methods

Pilot operation: The NF pilot can host two 4 inch spiral wound elements (Filmtec NF 270-400) to treat up to 80 L/h of brine in feed and bleed mode under 10 bars. During operation, the brine concentrates in a recirculation loop for 30 minutes with a constant concentrate flow withdraw. To maintain a stable flux and keep organic deposition on the membrane under control, the recirculation loop is kept at a high flux of 4 m^3/h. After that the content of the loop is flushed out; and the membranes rinsed with a mixture of fresh brine and air for 1 minute aiming at removing any material deposited on the membranes with high shear.

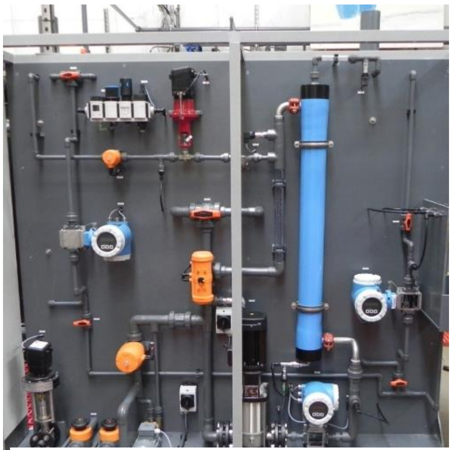
Figure 8: NF pilot in Andijk

Membrane autopsy: The membrane autopsy was performed on an 8 inch (Filmtec NF 270-800) membrane module which had run for eight consecutive months under similar conditions as described above. Within a day, a spiral would element was taken out of operation, cut open and unwounded for samples to be collected at five positions on a random membrane sheet with sterilized tools. After dissolution of the fouling material in an ultrasonic water bath, samples were analyzed for biomass parameters: ATP, TOC and inorganic carbon (IC).

Results

Goal 1: Separation properties

Averaged weekly sample analysis of the influent brine, permeate and concentrate are provided in table 5. The quality of analysis data does not allow to make the mass balance. However the retention percentage over the membrane could be calculated between the feed and the permeate. Despite the good overall retention of DOC and sulphate, respectively 90 and 73%, the reuse of the NF permeate in the SIX© process would bring the contamination of the fresh salt solution above 8%. In addition, the chloride content of the produced permeate is too low for direct reuse and would need to be to be concentrated a minimum of three times.

Table 5: analytical data NF pilot

	Na (g/L)	Cl (g/L)	SO_4 (g/L)	HCO_3 (g/L)	DOC (mg/L)
SIX© brine	10 ± 5	9.2 ± 5	8.2 ± 2	4 ± 4	460 ± 400
NF permeate	9 ± 4	11 ± 5	2.8 ± 2	4.4 ± 4	60 ± 40
NF concentrate	14.6 ± 6	8.4 ± 4	20 ± 7	4.3 ± 3	1100 ± 800
retention %	29%	18%	73%	22%	90%

Goal 2: Operational parameters

Figure 8 displays the operational data from the pilot when treating 1,5m^3 of brine with a recovery of 73% and a constant pressure of 10 bars. Every 30 minutes, a flush was performed with air and the brine to disturb any cake layer that could have formed on the membrane surface and to reestablish the flux. After 2000 minutes, the brine was refreshed for a new batch. Overall an average flux of 3,7 LMH was achieved.

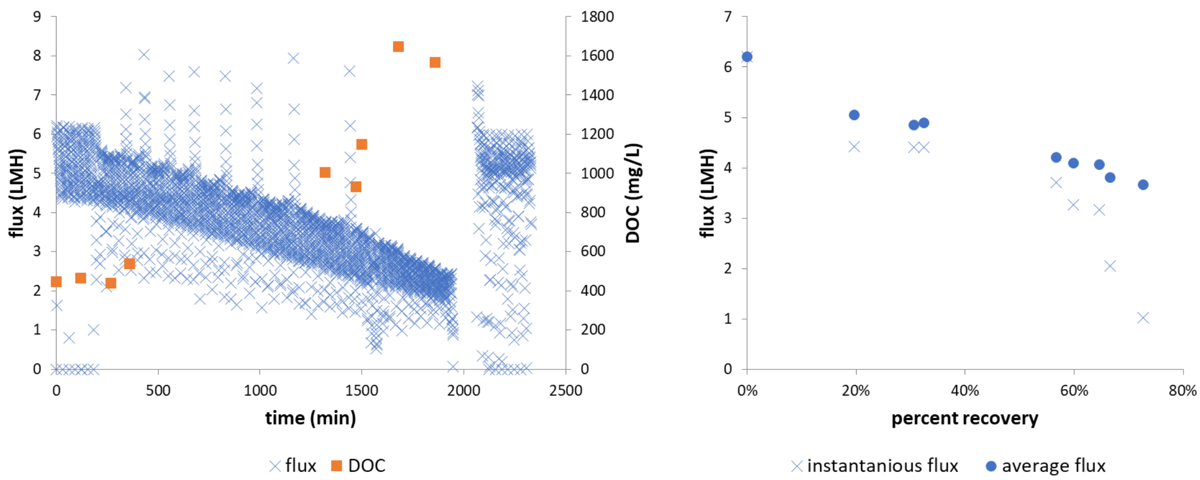

Figure 9: Operational data NF pilot

Goal 3: Fouling assessment

After 8 months operation, an autopsy of the Filmtec NF 270-800 element was performed to determine the type and degree of pollution (biofouling and scaling). At opening, a substantial deposition of material was observed on the inflow and outflow side of the membrane element and on the membrane / spacer before and after opening of the membrane module (Figure 9). The accumulated material felt slimy and soft (not granular) and was easy to remove from the membrane via scraping.

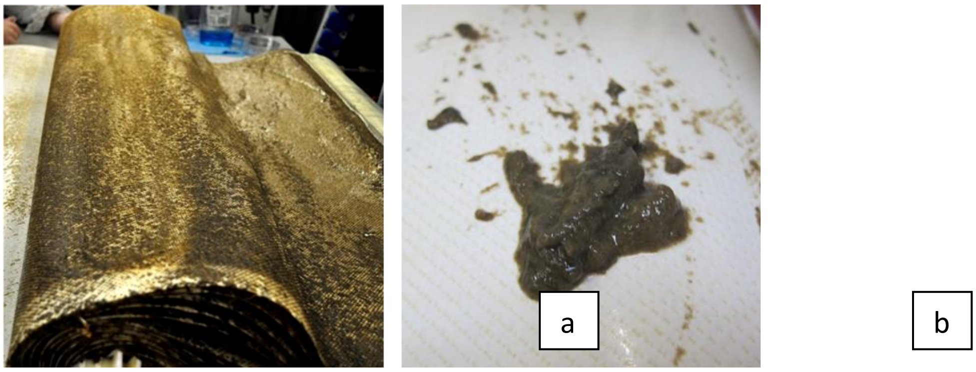

Figure 10: membrane autopsy, visual observation of a- NF spiral wound element treating SIX© brine for 8 months, and b- scraping of accumulated material

Samples were taken along the length of the membrane to determine the biomass concentration. The membrane coupons were pretreated in an ultrasonic water bath for the analysis of biomass parameters. Adenosine triphosphate (ATP) was measured as a biomass parameter, which is a measure of the active biomass concentration. The average concentration of active biomass on the membrane was 140 ± 67 ng ATP / cm ^{2}. With increasing distance to the feed side of the membrane, the ATP level decreased (Table 4). The TOC content was on average, 1182 µg C / cm 2 and the inorganic carbon content (IC) was on average, 38 µg C / cm ^{2}. The ATP content and TOC material being predominantly located on the feed side is a common sign of biofouling.

Table 6: membrane sample analysis

location	ATP	TOC	IC
	pg ATP/cm2	µg/cm2	µg/cm2
0 – 3 cm feed side	244.700	2.202	60
25 cm	152.500	1.420	46
45 cm	118.700	649	18
70 cm	118.600	994	42
90 – 93 cm outflow side	63.100	643	28

This membrane element has the highest ATP and TOC content of all membrane autopsies performed at Wetsus (up until 2011, around 200 membrane elements from around 30 installations).

Electrodialysis

As an alternative to NF, ED was piloted to extract, concentrate and recover NaCl and reduce fouling. This treatment scenario assumes the effluent diluate to be suitable for return to Lake IJssel, as it would be clear of most of the added chemicals.

Specific goals for this pilot study are:

1- Define the separation properties of monovalent selective and standard types of ED membranes
2- Define the operation parameters for stage 1, monovalent selective stack: ion passage per membrane area, current density, reversal frequency, CIP frequency,
3- Define the long term operability including aging effect on the membrane and possible fouling.

Material and methods

Pilot operation: The ED pilot consists of a stack provided by Eurodia (EUR6B-50) and is equipped with 50 cell pairs of Neosepta CMXsb and Neosepta ACS monovalent selective membranes allowing direct treatment of the SIX© brine for NaCl recovery.

Operations occur either in batch or feed and bleed mode, under a constant potential of 45V. Fouling of the membranes is controlled by reversing the polarity on a daily basis and preventative CIPs are performed weekly by recirculating base (NaOH at pH 11) then acid (HCl at pH 3) solutions through the membranes for 30 minutes and rinsing with water in between and at the end. A single sulfamic acid solution at 20 mS/cm circulates through the electrode compartments of the stack as electrolyte solution..

Figure 11: Electrodialysis pilot

Episodes of fouling are usually noticeable as they induce an increase in electrical resistance over the membrane which in turn causes a decrease in current density. However, several operational parameters directly influence the current density, such as the conductivities of all streams including the electrolyte, and the operational temperatures. Therefore to investigate the condition of the membranes, demineralization tests were frequently performed after completing a CIP. Demineralization tests allow to assess the ion exchange capacity of the membranes under replicable conditions (with the exception of temperature). Two 30 mS/cm NaCl solutions (each 60 L, prepared in RO water) were recirculated in the diluate and concentrate tanks, and the stack was operated under 45V applied for 30 minutes. The demineralization rate was then recorded to assess the exchange capacity of the membrane over time. In addition, 16 months into operation, the state of the membranes (ACS and CMXsb) were assessed by performing a destructive characterization over one cell pair. Details of the characterization tests were previously published in Vaudevire *et al* (2019) [6].

Results

Goal 1: Separation properties

During feed and bleed operations of the pilot, the diluate and concentrate bleed independently from each other. The diluate bleeds on a low limit set depending on the quality of the influent SIX© brine between 10 and 15 mS/cm, which usually leaves less than 1 g/L of chloride in the diluate effluent being disposed of. The concentrate bleeds on a set value of 90 mS/cm, which correspond to a chloride concentration between 25 and 30 g/L. The averaged influent and effluent values, presented in table 7, confirm the successful extraction and concentration of NaCl from the SIX© brine with ED.

Table 7: ion transport first stage ED

	Conductivity (mS/cm)	Na (g/L)	Cl (g/L)	SO_4 (g/L)	HCO_3 (g/L)	DOC (mg/L)
SIX© brine	40	13.2	12.8	6.2	5.0	381
Concentrate ED	107	37	48	0.21	10	5.4
Diluate ED	14	4.6	0.9	6.7	1.8	370
Retention %		34%	7%	100%	35%	89%

Goal 2: Operational parameters

The operational capacity of the process treating the SIX© brine, was defined with batch runs: a brine volume of 200 L and a concentrate volume of 60 L recirculated over the stack for 80 minutes under a constant voltage of 45 V (0.9 V/cell pair). The operational data retrieved from the pilot are displayed in figure 11 and the calculated transfer of salts is presented in table 8. A demineralization rate of 50% was achieved with an ion passage of 7.04 eq/(h m^2) and under an average current density of 242 A/m^2.

Table 8: salt transport during batch trial

	unit	chloride	sodium	bicarbonate	sulphate	nitrate
Initial conditions						
SIX© brine	mg/L	5150	6660	2300	4300	44,6
concentrate	mg/L	18000	14000	408	1200	2,46
Final conditions						
diluate	mg/L	820	2860	1600	4500	2,52
concentrate	mg/L	22000	16700	1800	930	83
Transport						
Extraction	eq/(h.m^2)	6.35	8.82	0.65	-	0.04

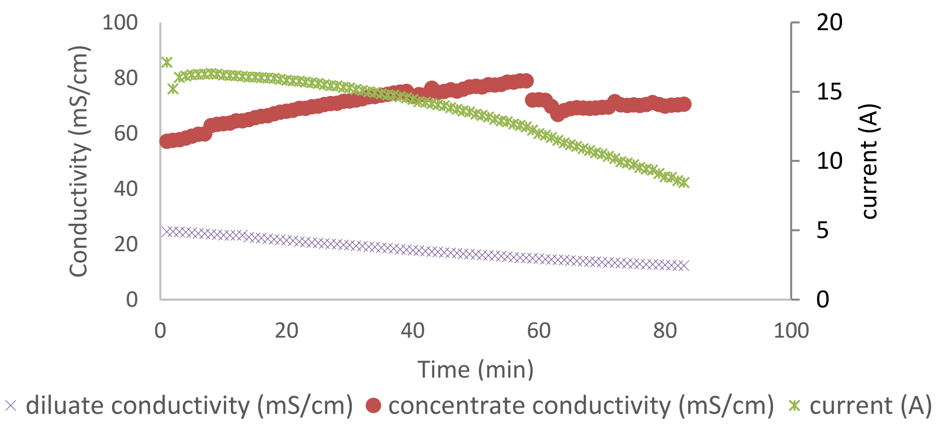

Figure 12: operational data obtained from the pilot during batch trial

Goal 3: Long term operability

Figures 13 and 14 depict 350 continuous hours of operational data retrieved from the pilot. Over time, the concentrate conductivity in red reaches its high value point of 90 mS/cm before bleeding 30 L of NaCl solution, immediately replaced by 30 L of RO water. The diluate in blue reaches the low value point fixed between 12 and 18 mS/cm before bleeding 60L of chloride free brine while replacing this with the same amount of SIX© brine. Due to this feed and bleed operation mode, the current density varies widely and overall doesn't reach the average 242A/m^2 defined earlier. This is however not representative of continuous operation but designed to follow the membranes properties over time. Interestingly, the data show that episodes of fouling can occur on a single side of a membrane as is the case between hour 50 and 150 (figure 14). During this time, the average current density differs between two reversals, indicating one side has a higher resistance due to fouling. This is also noticeable from the slower conductivity transfer in figure 13. The membranes fully recover after the CIP at hour 150.

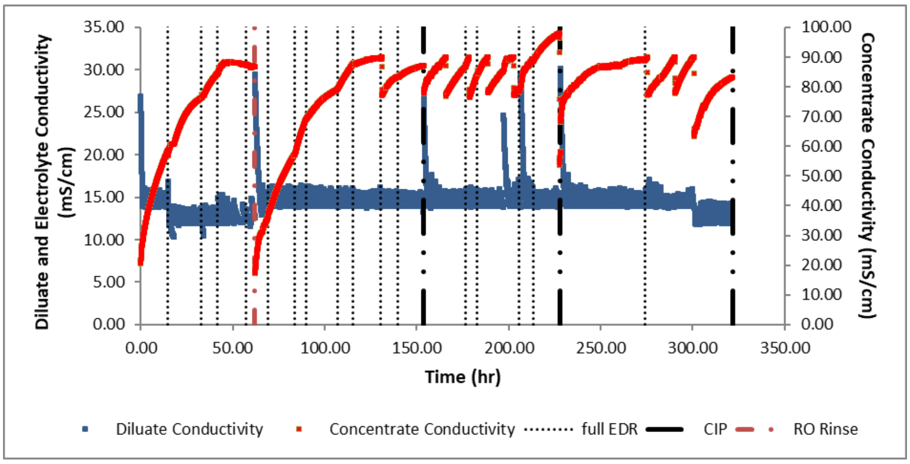

Figure 13: Operation data ED (conductivities)

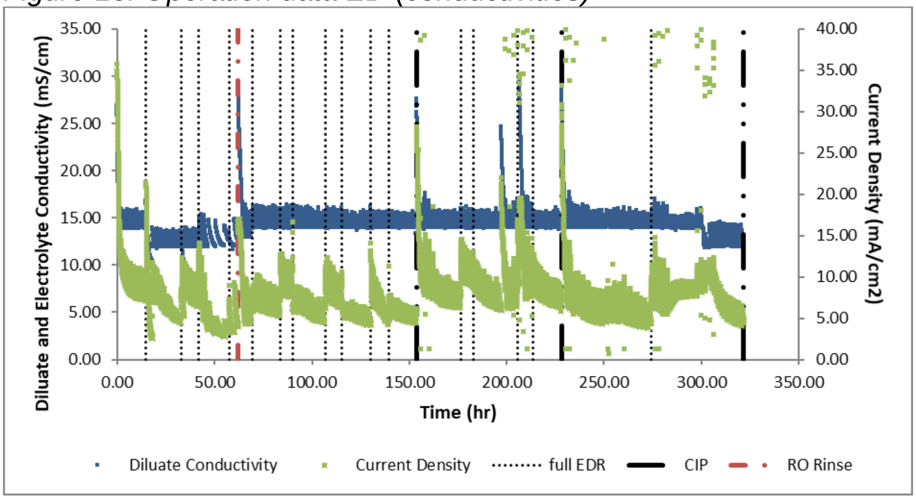

Figure 14: Operation data ED (diluate conductivity versus current density)

As mentioned previously, in order quantify the decrease in exchange capacity of the membranes over time, demineralization rates were calculated under reproducible conditions after each CIP over the full period. A samples of these demineralization test results are pictured in figure 15. Over 3 years of operation, a steady decrease in exchange capacity is noticeable which is estimated at around 30%.

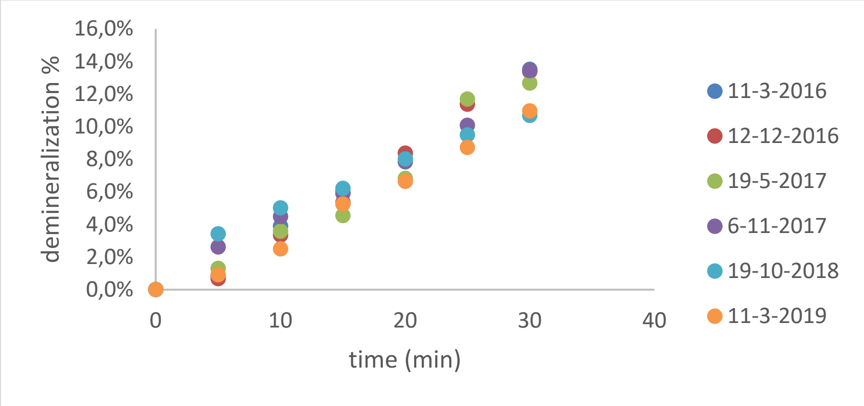

Figure 15: results from a few demineralization tests selected over a full period of operation

Finally the results of the autopsy evaluation of the membranes are displayed in table 9. It shows a comparison of the physical properties of new membranes and membranes after 1800h of continuous operation. While the properties of the cation exchange membranes (CMX) are relatively unchanged. The anion exchange membranes (ACSsb) suffers a significant increase in electrical resistance: 57% in NaCl,85% in $MgSO_4$. Anion exchange membranes are more susceptible to fouling than the cation exchange membranes due to the negative charge on the DOC.

Table 9: Characterization of the membranes

	thickness (µm)	permselectivity (%)	resistance (Cl/Na) (Ω.cm²)	resistance (SO_4/Mg) (Ω.cm²)
ACSsb new	131	86.47 ± 0.54	4.27 ± 0.10	18.67 ± 017
ACSsb 1800h	126	86.39 ± 0.41	10.04 ± 0.35	87.04 ± 7.09
CMX new	135	90.2 ± 0.03	3.25 ± 0.01	2.38 ± 0
CMX 1800h	189	100 ± 0.22	2.38 ± 0	8.21 ± 0.08

Pilot evaluation of volume reduction and ZLD (batch)

VSEP

The VSEP was investigated as a volume reduction step for the SIX© brine prior to evaporation in a logic of ZLD. Two main requirements were stipulated for the membrane preconcentration step: a conductivity below 1 mS/cm for the permeate to be discharged or reused ahead of the SIX and robustness of the process. The vibration induced in the VSEP process at the surface of the membrane creating a turbulent environment were thought to hinder the formation of an organic cake layer, and as a result bring better control of flux and reduce permanent fouling.

Goal 1: determine the optimized recovery and flux for the production of a low conductivity permeate.

Goal 2: assess the irreversibility of the fouling

Method:

The pilot (figure 18) comprises a few filtration disks for a total membrane area of 1,56m^2 mounted on the vibration system. The membrane in place is Hydranautics ESPA and the total volume of brine tested is 150 L. The concentrate is recirculated while the permeate is removed from the system. The volume reduction of the brine was evaluated in two steps: one performed at 34,5 bars and one at 62 bars. The trial is stopped when the permeate flux drops below 8 LMH.

CIPs are performed with warm water (53 to 59°C) followed by a rinse at pH 2,5 and one at pH 11, all under 4 bars pressure.

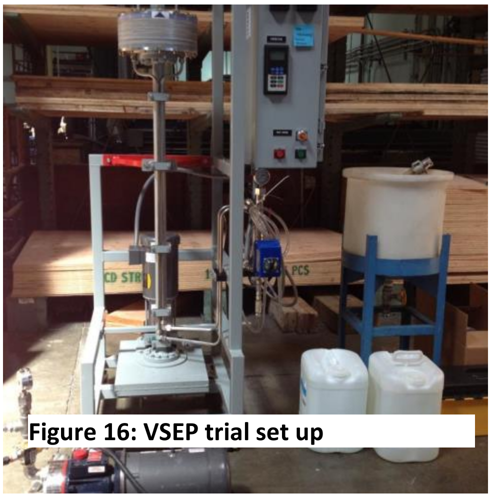

Figure 16: VSEP trial set up

Results:

Goal 1: The average and instantaneous fluxes over the two steps of treatment are displayed in figure 18 and process parameters are summarized in table 9.

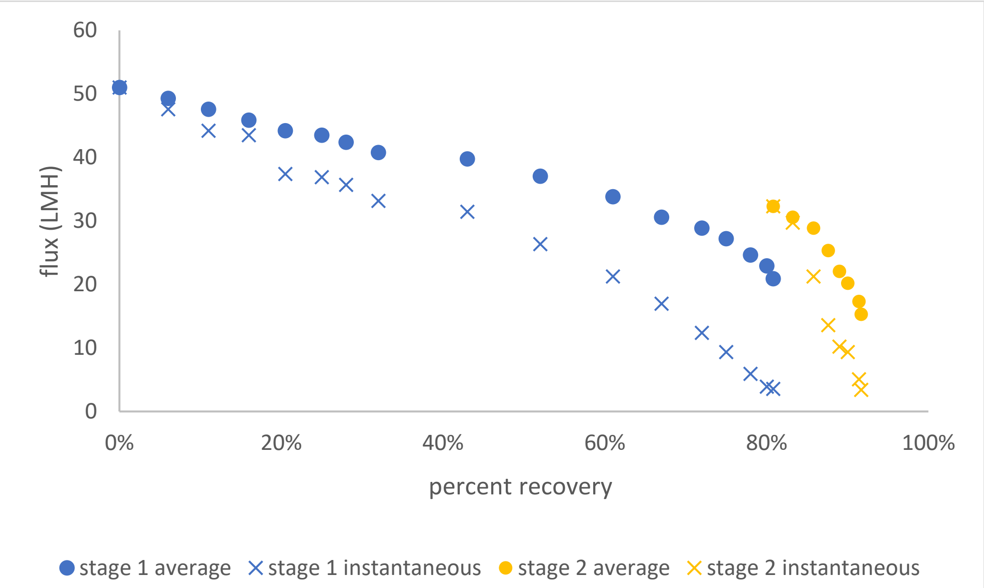

Figure 17: VSEP flux vs permeate recovery

Table 10: process parameters resulting from the tests

	Pressure	Average flux	% recovery
Stage 1	34,5 bars	20,9 LMH	80,8%
Stage 2	62 bars	15,6LMH	57,0%

The quality of permeates and concentrates over the two stages are detailed in table 10. It shows that over the two steps, sulphate and DOC was retained to over 99%, sodium to over 97% and chloride to over 92%. A visual impression of each sample is given in figure 19.

Table 11: VSEP influent and effluents qualities

Sample	SIX© brine	Concentrate VSEP1	Permeate VSEP1	Concentrate VSEP2	Permeate VSEP2
pH	7,1	7,2	7,4	8,3	7,3
Conductivity (mS/cm)	20	72	0,75	100	2,2
Chloride (g/L)	2,2	18	0,15	27	0,46
Sodium (g/L)	5,4	28	0,11	54	0,51
Sulphate (g/L)	8,2	38	0,055	120	0,14
Bicarbonate (g/L)	1,2	5,9	0,034	-	0,1
Nitrate (mgN /L)	<2,5	<2,5	0,95	<0,5	<2,5
DOC (mg/L)	660	1700	5	4200	11

Figure 18: From left to right, the initial brine, VSEP standard pressure permeate, VSEP standard pressure concentrate, VSEP high pressure permeate, and VSEP high pressure concentrate

Goal 2: The direct effect of the vibration on long term operability could not be assessed as part of this short trial, however at the end of each stage a CIP of the membranes was conducted to determine if the membrane flux loss due to fouling could be recovered.

Table 12: CIP conditions and flux recovery in the VSEP pilot

	Temperature	pH	Flux	% of initial flux
Initial conditions	25ºC	7	136 LMH	100%
After stage 1	56 ºC	7	81,6 LMH	60,0%
After low pH rinse	53 ºC	2,5	124 LMH	91,3%
After high pH rinse	53 ºC	11	128 LMH	93,8%
After stage 2	59 ºC	7	102 LMH	75,0%
After low pH rinse	55 ºC	2,1	98,6 LMH	72,5%
After high pH rinse	53 ºC	11	124 LMH	91,3%

The cleaning regime applied was successful for restoring the membrane properties to within 10% of its original flux, which is considered normal. After stage one the acid rinsing alone was sufficient to restore the membrane properties indicating that organics were probably the cause of the fouling. This was not the case after the second stage which required both high and low pH rinsing to restore the flux, indicating that the salts might have participated to the fouling as well.

RO integrated

Alternatively to the VSEP concept, standard spiral-wound RO membranes under ultra-high pressures were trialled as treatment for SIX© brine. In order for the membranes to sustain the brine composition, an extensive pre-treatment with coagulation and ceramic UF was required for DOC reduction upfront as depicted in Figure 19. The goal here was to determine the optimized recovery and flux and the quality of the effluents.

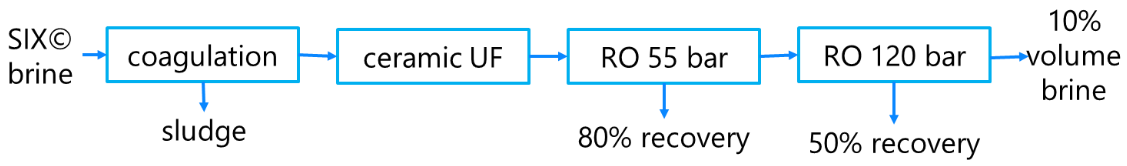

Figure 19: schematic of the ultra-high pressure RO and pre-treatment system

Method:

The full treatment train was investigated on pilot scale with the following settings:

- Coagulation: The dosage of $FeCl_3$ between 1 and 3 g $FeCl_3$/L occurs directly into the stirred feed vessel with a retention time of 40 minutes. The process will produce a sludge waste stream.
- Ceramic UF: The ceramic membranes (pore size of 0.1µm) operate under constant pressure of 3 bars. To keep fouling under control, rinsing with feed water at high cross flow velocity (2 to 5 m/s) is frequently applied to reduce formation of a cake layer at the surface of the membranes. When necessary the membranes are backwashed with NaOH solution at pH 12.
- RO first stage: The first stage of RO treats the permeate from the UF at a constant pressure of 80 bars. Membranes used are regular sea water RO modules (Nitto Hydronautics).
- RO second stage: The second stage of RO further treats the concentrate from first stage RO with similar membranes but at an increased pressure of 120 bars.

Results:

After coagulation and UF, the DOC in the brine was reduced to 56 mg/L (75% removal) and an average flux of 200 LMH was reached on the UF. More details on coagulation performances with SIX© brine are given later in this report. The fluxes over time over RO stages 1 and 2 are depicted in figure 20 and process parameters summarized in table 13.

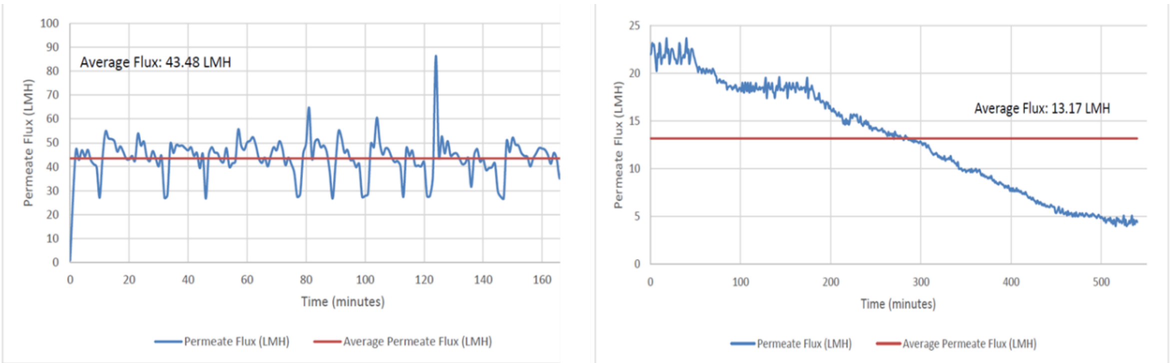

Figure 20: flux over time RO stage 1 (left) and RO stage 2 (right)

Table 13: process parameters resulting from the tests

	Pressure	Average flux	% recovery
Step 1	80 bar	43,48 LMH	80%
Step 2	120 bar	13,17LMH	50%

The detailed composition of the permeates and concentrates over the two stages are given in table 14. DOC and sulphate was retained above 99%, chloride and sodium over 94%. Both permeates (figure 21) had clear appearances.

Table 14: RO influents and effluents qualities

Sample	SIX© brine	Perm RO1	Conc XRO1	Perm RO2	Conc RO2
pH	8,5	6,7	7,8	6,9	7,8
Conductivity (mS/cm)	-	0,2	-	1,6	-
Cl (g/L)	2,5	0,10	19	0,14	42,3
Na (g/L)	5,0	0,73	23,4	0,98	51,4
SO4 (g/L)	5,6	0,03	22,6	0,04	48,8
HCO3 (g/L)	1,2	0,004	1,1	0,005	0,34
DOC (mg/L)	230*	1,7	282	1,2	975

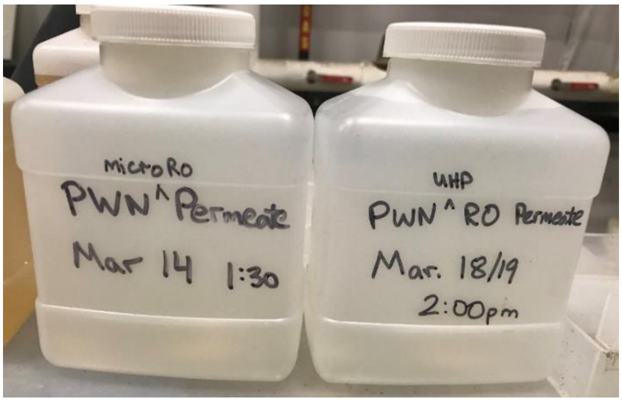

Figure 21: permeates stage 2 and stage 1 from left to right.

Evaporation – crystallization process selection (desk study)
The selection of the evaporation method, among the ones described earlier, was based on their energy efficiency. Providers of the different technologies were asked for a projection of the energy demand treating 30 m^3/h of the SIX$^©$ brine as described in table 3. These are summarized in table 15. The DyVaR, based on the MVR concept was found not only more energy efficient but also free of thermal energy.

Table 15: Energy requirement of the different evaporation technologies, as projected by technology providers

System	electrical energy requirement for 30 m^3/h design (kW))	nat. gas energy requirement for 30 m^3/h design (kW)	total energy requirement (kW) for 30 m^3/h design
Atmospheric	x	16773	16773
HDH+ Thermal crystallizer	204	8816	9020
MVR	1500	x	1500

Evaporation – crystallization with DyVar

PWNT participated in the development of the DyVaR by implementing and operating the first pilot equipment of the new technology. The DyVaR was designed as a cost effective ZLD solution for utilities with low energy requirements and cheaper construction material. A particularity of the DyVaR compared to commercial MVR is the use of evaporation cyclones with fixed design that can be multiplied to adapt to the flow rather than scalable evaporation columns. The research program included the investigation of a controlled precipitation to separate the recovery of different salt species, details of which can be found in [7], [8].

In this feasibility study, the focus was on the recovery of water to reach ZLD with the following specific goals:

1- Determine the composition of the condensate and salt crystals produced.
2- Establish the treatability of the brine to ZLD and the impact of concentration factor on its rheological properties.

Material and methods

Pilot operation: The DyVaR unit in Andijk consists of 5 cyclones with a capacity of 280 to 320 l/h. The applied compressor frequency is 65%, which results in a stable pressure over the cyclones between -0,17 and -0,28 bar. The temperature of the brine in the recirculation loop is maintained at 92°C and the pump frequency at 80%. When foaming occurs, 60 mg/L of silicon oil based anti-foam agent is dosed inside the unit.

Figure 22: picture of DyVar pilot at PWNT (5 units)

Results

Goal 1: Composition of end products

Regular operations of the DyVaR were performed concentrating the SIX© brine with a factor 6, before any salt crystallization would occur. At this concentration factor (CF), the pilot reduced the SIX© brine from 275 L/h to 45 L/h and offered 230 L/h of water recovery that could be re-injected upstream the SIX©. The quality of the concentrate and condensate obtained at this ratio are displayed in table 16. The DyVaR pilot during its operation has proved its ability to treat various qualities of brines without any sign of fouling/scaling, making it a robust process.

Table 16: Quality of the SIX© brine, condensate and concentrate of the DVR pilot at a concentration factor of 6.

	Chloride	Sodium	Bicarbonate	Sulphate	TOC
	mg/L Cl	mg/L Na	mg/L HCO_3	mg/L SO_4	mg/L C
SIX© brine	17000	15000	5700	7200	380
DyVaR Condensate	2	1.3	15	1	0.9
DyVaR Concentrate	91200	86000	19000	39000	1900

Goal 2: treatability of the brine to ZLD and assessment of the rheological changes

The second part assesses the change in rheology in the SIX© brine as the concentration factor increases. This assessment was carried out with ED diluate (SIX© brine that underwent one stage of monovalent selective ED) in the absence of chloride (table 16) is still informative but should be conducted again on SIX© brine. 12 m^3 of ED diluate was concentrated to the minimal volume the test unit would allow (250 litres), reaching a concentration factor of 45 ~ 50. To continue the investigation below the pilot minimum set up point, the 50 times concentrated brine was carried over to a bench scale test and boiled on a heated plate (stirred). During the transport to the lab, the temperature of the solution dropped and precipitation occurred which resulted in a first loss of crystal salts. The supernatant was further concentrated four times bringing the concentration up to a factor 200 approximately. The viscosity of the liquid at this point made it impossible to further carry on with the testing.

A theoretical precipitation model was used to define the thresholds at which each compounds starts precipitating and the composition of the concentrating brine at process conditions (90°C) described in table 16:

- At a CF 11, Na_2SO_4 starts precipitating upon cooling down to 20°C
- At CF 24, Na_2SO_4 reaches oversaturation at process temperature within the DyVaR
- At CF 30, Na_2CO_3 starts precipitating upon cooling down to 20°C
- At CF 113, Na_2CO_3 reaches oversaturation at process temperature within the DyVaR

Table 17: Model of brine composition under increasing concentration factors at 80°C

	Analysis at 20°C		Model prediction of the concentrating brine composition			
Sample	ED diluate	DyVaR concentrate x 50	Concentrate X24	Concentrate X50	Concentrate X100	Concentrate X200
Cl (g/L)	0,2	11	4.8	10	20	40
Na (g/L)	6	66.2	144	144	144	144
SO_4 (g/L)	10	62	240	240	240	240

HCO_3 (g/L)	2.2	12,4	52.8	110	249	249
DOC (g/L)	0.266	11.3	6.4	13	27	53
TDS (g/L)	-	-	448	517	680	726

The rheology characteristics of the brine under increasing TDS concentration were analyzed at process temperature (80ºC) and are displayed in figure 23. Viscosity at 726 g/L TDS is not shown in the graph for representation propose as it reached 56.93 mm^2/s.

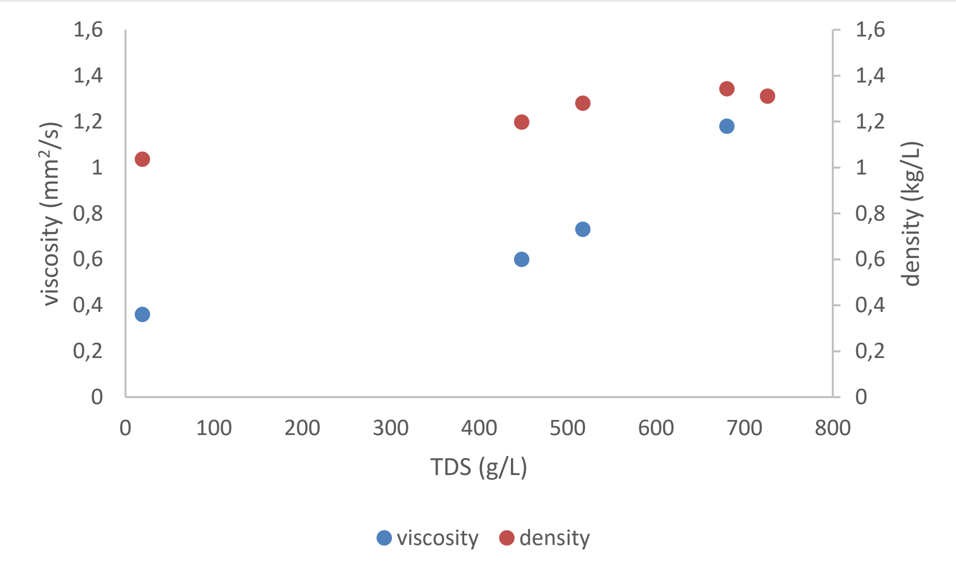

Figure 23: increase in viscosity and density in the brine with increasing TDS

Up to a TDS concentration of 680 g/L concentrating the brine did not induce severe rheological changes at boiling temperature. Passed this concentration however, the liquid at boiling temperature started acting like a syrup, and viscosity drastically increased. This maybe attributed to the increasing DOC ratio or the crystals formation unable to escape the liquid phase. The consequences of the increasing TDS up to 680 g/L on the boiling point increase of the liquid and the energy requirement for the compressor, in a MVR process are calculated in table 17.

Table 18: characteristics of the brine at CF 0/ 24/ 50/ 100 and 200 analyzed at 80 ºC, and compressor power requirement

Analyzed at 20˚C	Modelized at 80˚C	Calculated		
TDS	**TDS**	**Boiling point increase (BPI)**	**Pressure differential compensating for the BPI**	**Theoretical compressor power required**
(g/L)	(g/L)	°C	bar	kWh/m^3 brine
19	19	1.12	0.04	1.23

-	448	2.91	0.10	6.33
163	517	4.26	0.145	9.73
-	680	5.18	0.174	12.17

<u>Bench scale evaluation DOC removal</u>

Chemical coagulation
Chemical coagulation was investigated for the removal of DOC prior to membrane treatment. The goal was to estimate the DOC removal of two different coagulants: ferric sulphate and aluminum chloride at various doses.

Material and method:
Jar tests were performed with 1 L of SIX© brine adjusted to pH 5. After addition of the coagulant, the mixing velocity was set on 200 rpm for 5 minutes of rapid mixing, then 45 rpm for 45 minutes of slow mixing prior to sedimentation.

Figure 24: Jar test in Andijk. Jars are numbered 1-6 from left to right

Results:
The results presented in table 16 show that better DOC removal is achieved with ferric sulphate, up to 68% at a 6 mM dose. Follow up experiments using higher doses could not improve DOC removal further. The volume of sludge produced after several hours settling was estimated to be 10%.

Table 19: final concentrations coagulation experiment

				Final Concentrations (mg/L)				
Coagulant	**Jar Number**	**Amount (metal, mol/L)**	**Amount (mg/L)**	**TOC**	**Fe**	**SO4**	**Cl**	**TOC removal (%)**
Control	1	0	0	309	0,643	7231	13,2	6
Ferric Sulphate ($Fe_2(SO_4)_3$)	2	0,0015	279	266	15,2	7557		19
	3	0.003	558	138	11,6	7434		58
	4	0.006	1116	105	76,5	7696		68
Aluminium Chloride ($AlCl_3$)	5	0.001	135	309			8,92	6
	6	0.004	540	254			10,1	23

Nyex adsorption - electrochemical regeneration
Nyex was tested as part of DOC2C's promotion of SME on Lake IJssel water and SIX© brine. Specific goals of this test on SIX© brine were the determination of DOC and color reduction from the SIX© brine under different operational conditions.

Material and method:
Two bench scale types of processes were used in this trial:

- Nyex TM 1-20 <u>A system</u>, combines the adsorption of DOC on the surface of the Nyex material with electrochemical oxidation occurring simultaneously. It operates at low current densities: 2,5 mA/cm² was applied for the brine trial

- Nyex TM 1-20 E system, designed to treat water with heavier loads of organic matter, which produces higher concentrations of OH· radical, hence relying more on oxidation rather than adsorption for the removal of DOC. The applied current density in this trial was 25 mA/cm2.

Two methods were used to remove the bicarbonate from the brine prior to the treatment: a treatment over the ED for monoselective ion removal, and acidification to pH 1 or 2. Trials were conducted by recirculating the brine over the Nyex bed for 2 to 28 hours at flow rates between 2 and 20 l/h. Two main performance indicator are used in this preliminary study: DOC and color removal.

Results:
Color removal (assessed visually) was achieved under all conditions. An example is shown in figure 16. The initial sample on the left was recirculated over the E system for 2 hours at a flow rate of 2L/h with samples taken after 15, 30, 60 and 120 minutes; full color removal was achieved during the first 15 min.

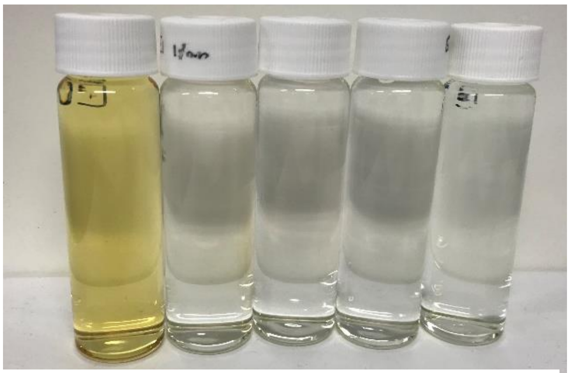

Figure 25: color removal from SIX(c) brine with Nyex

Results obtained from the E system for DOC removal are displayed in table 9. Under various process conditions applied, the DOC removal remained around 25% with full color removal. Despite ED treatment and acidification of the sample, some remaining carbonate could be reacting with the OH· radicals and hindering the efficiency of the process.

Table 20: E system trial results (under constant current density 25 mA/cm^2)

Trial number	Brine	Flow	Trial duration	DOC reduction
E 1&2	SIX© brine pH 2	2 / 20	2h	25-26%
E 3&4	SIX© brine pH 2	2/ 20	4h	25%
E 5	ED pH 1	2	4h	24%
E 6	ED pH 1	20	4h	22%

The maximum DOC removal (52%) was achieved with the combination of the two systems in series with a brine acidified to pH 1 and recirculated for 28 hours.

Summary technical feasibility

NaCl recovery & discharge
In this strategy, the NaCl is extracted from the brine to be returned to the SIX© regeneration process; so the chloride free brine can safely be discharged back to Lake IJssel upon acquisition of a permit by the environmental authorities. ED demonstrated great ability to do so. Under the pilot condition, ED consistently reduced the chloride level in the brine under 1 g/L and allowed the recovery of over 90% of it in a sufficiently concentrated solution for its direct reuse. Passage of sulphate, DOC and bicarbonate to the concentrate was limited to respectively 0%, 11% and 65%. The operational parameters retained to scale up the process were an average current density of 240 A/m^2 allowing the passage of 7 eq/(h.m^2). After three

years of operation the membrane showed a 30% reduction in exchange capacity which should be accounted for in a full scale design.

Zero liquid discharge
This strategy aims at the complete recovery of water in order to only dispose of solid waste or possibly reuse as road salts for example. It will only be implemented if no permit for discharge is granted. Therefore it requires robustness and redundancy as, in case of system failure, storage of the SIX© brine is the only option. To seek this robustness, a first concept of treating one hundred percent of the brine volume with evaporation and crystallization was envisaged. However the reality of energy requirements made this option unfeasible. In a new concept, as it is common practice in ZLD, the first volume reduction will be operated over membrane treatment, with NF and RO trailed as part of this report. To ensure the durability of the membranes, pre-treatment for DOC removal was investigated as well with coagulation and adsorption oxidation. Finally the concentrate from the membrane treatment will be brought to full water recovery and crystallization in an evaporation system. The robustness of the membrane technology chosen as well and the energy efficiency of the evaporator crystallizer were the main factors driving the selection of a technology.

Pre-treatment for DOC removal
Two possible technologies were investigated for DOC removal,
- the enhanced coagulation could achieve up to 70% of DOC removal but produced 10% in volume of sludge (before dewatering) to dispose of.
- The adsorption-oxidation process doesn't produce any waste stream but could only achieve 25% of DOC removal possibly due to the presence of carbonate in the brine.

Membrane volume reduction
Three options were assessed:
- NF reached 80% recovery treating the SIX© brine; but despite the implementation of a high recirculation loop for the control of cake layer formation and fouling, could only reach a low flux of 4 LMH under 10 bars. In addition, the concept is only viable if the recovery of the permeate as a fresh sodium chloride solution is possible. The pilot study found the concentration of chloride to be too low for direct reuse, and the passage of sulfate (27%) would lower the purity of the fresh salts with possible repercussions on the SIX© adsorption kinetics. Finally, the fouling rate would imply a high turnover of membranes. Therefore NF was not considered further in this report.
- RO in a VSEP process could treat the SIX© up to 90% recovery in two stages. The first stage at a flux of 21 LMH under 34 bar and the second stage at a flux of 16 LMH under 62 bar. The combined produced permeate (stage 1 & 2) was found suitable for discharge or reuse in the drinking water treatment with a TDS content below 500 mg/L. The main advantage of this technology is the simplicity of a one process step design, which also reduces the risks of failure. The main foreseen disadvantage of the process would be the cost and single source of membranes packs. Long term operation still need to be investigated but the VSEP was further investigated for design and economic assessment.
- RO in an integrated design with pretreatment and ultra-high pressures could also treat the SIX© brine to 90% recovery in two steps. After a removal of 75% of DOC after coagulation and ceramic MF, the first step operating under 80 bar reached a flux of 44 LMH and the second step under 120 bars reached 13 LMH. The membranes used in the trial in the standard spiral wound configuration were of the same fabric than the ones used in the VSEP and achieved similar results. The combined permeate quality was kept below 900 mg/L TDS. The foreseen advantage of this process is the use of

standard membrane modules. The main foreseen disadvantage would be multiple steps and the production of 3 m^3/h of coagulation sludge (before dewatering).

Evaporation – crystallization

The selection of an evaporation technology was based on a desk study showing the superior energy efficiency of MVR processes compared to atmospheric and HDH evaporator. The trial in Andijk with the DyVaR, based on the MVR concept, confirmed the treatability of the SIX© brine past crystallization levels up to a TDS of 680 g/L at process temperature (assessed in the absence of chloride). Upon cooling down the final effluent resembles a slurry to dispose of and equals the accumulated amount of TDS fed to the system. The condensate contains less than 25 mg/L TDS and can be returned to the source of the drinking water process. Upscaling parameter for the DyVaR include the production of 50 L/h of condensate per evaporation cyclone.

The three technically viable strategies defined during pilot tests are summarized in figure 26. Details of each stream composition are given in tables 21 and 23.

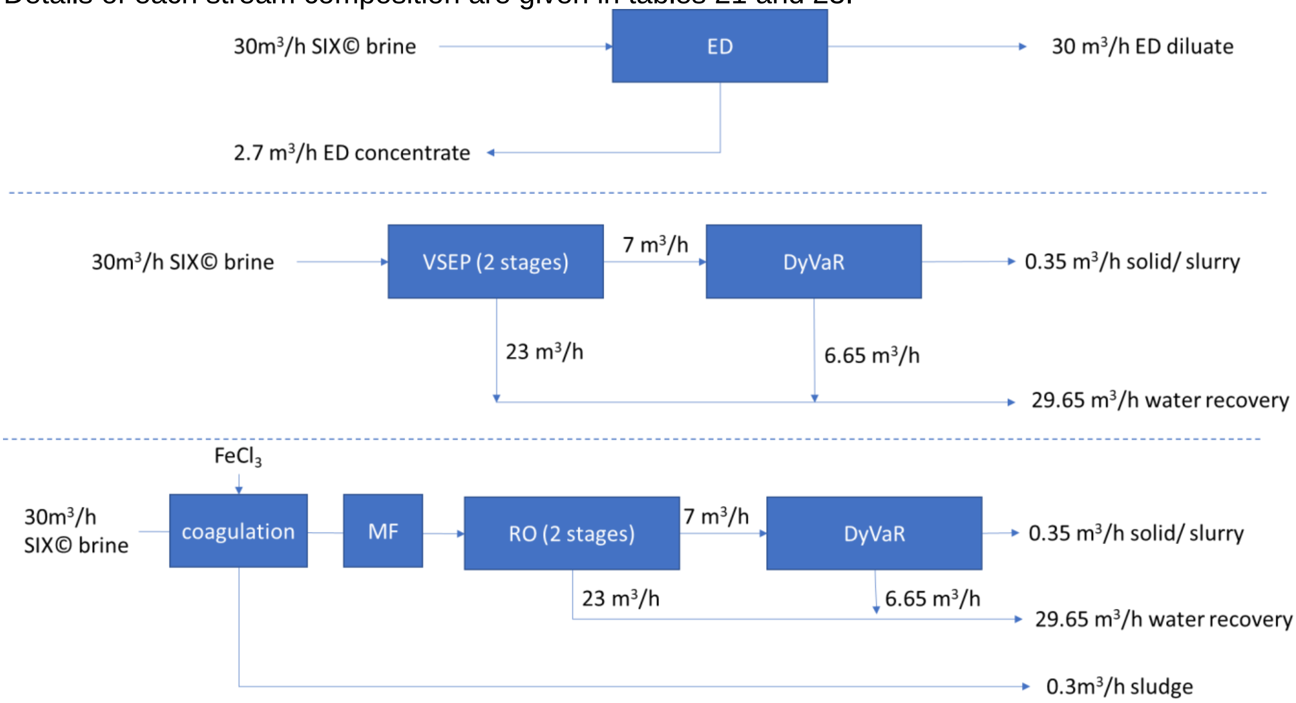

Figure 26: flow charts for the three brine treatment options

Financial feasibility assessment

In this next part, the implementation of the different strategies have been projected to the full scale and financially estimated.

ED for NaCl recovery and discharge of the treated diluate to Lake IJssel

Pilot tests established ED was suitable for the recovery of 90% of the chloride from the SIX© brine under an average current density of 240 A/m^2, resulting in an ion passage of 7 eq/(h.m^2). Under these condition, the treatment of 30 m^3/h of SIX© brine would require a surface area of 520 m^2. A design was proposed using a total of 5 stacks, rotating between 4 stacks in operation and 1 stack offline for CIP and maintenance for a total CAPEX estimated at 2 400 000 euros. A summary of the design is proposed in table 22 with estimated OPEX.

Table 21: Projected average stream qualities

Parameter	Flow	Sodium	Chloride	Sulphate	Bicarbonate	DOC	conductivity
Unit	m^3/h	g/L	g/L	g/L	g/L	mg/L	mS/cm
SIX brine	30	7	4	6	3	270	20
ED diluate	30	2.4	0.3	6	1	240	12
ED concentrate	2.7	51	41	<1	22	330	110

Table 22: process design

design parameter	unit	Value ED
capacity	m^3/h	30
min chloride recovery	%	90
final chloride in ED diluate	mg/L	200 to 900
concentrate production	% in volume of influent	9
membrane area	m^2	520
number of stacks	#	5
average current density	A/m^2	240
footprint	m x m	22 x 10
height	m	3.5
energy consumption	kW	310
chemicals : HCl NaOH	 kg HCl /week kg NaOH /week	 53 53
CAPEX	euro	2 400 000
OPEX[1]: Energy Membrane Chemicals Salt recovery	euro/y	(Total) 8 000 180 000 1 800 30 000 -220 000

Zero liquid discharge

The choice between the VSEP and XRO technologies is uncertain and should be define after long term pilot experiment. For the requirement of this report, the two options have been estimated. The pilot tests could establish that both pretreatment technologies were able to recover 90% of water from the SIX© brine with similar chemical compositions. The DyVaR

[1] *OPEX assumes € 0.08/kWh and € 14.5/gallon membrane cleaners

would further evaporate the concentrate with 95% of water recovery to only produce a solid/slurry waste. This design was made with extra capacity and redundancy to increase the reliability of the system.

Table 23: Projected average stream qualities

Parameter	Flow	Sodium	Chloride	Sulphate	Bicarbonate	DOC	conductivity
Unit	m^3/h	g/L	g/L	g/L	g/L	mg/L	mS/cm
SIX brine	30	7	4	6	3	270	20
Coagulation sludge	3	(before dewatering and only in the case of an integrated RO)					
Water recovery	29.85	0.4	0.2	0.05	0.1	2.7	<0.5
DyVaR slurry	0.15	-	-	-	-	-	-

After cooling down, most of the DyVaR slurry content will crystalize and produce 645 kg/h of solid waste containing, according to the precipitation model, 37% of sodium sulphate, 28% of sodium chloride, 34% of sodium carbonate and 1% of organic matter.

VSEP / integrated RO

In the proposed design, both membrane concepts would treat the SIX© brine up to 77% recovery and reduce the waste brine to 7 m^3/h.

- The VSEP operates as a unit, in which fouling is kept under control by the action of the vibratory shears. A proposed design is based on a first stage with 13 packs (membrane area ≈ 1615m^2) at a flux of 20 LMH and a second step with 2 high pressure packs (membrane area ≈ 210m^2) at a flux of 15 LMH. For OPEX calculation, the lifetime of the membranes is estimated to 2 - 2.5 years and the average price of a pack is € 70 000.
- The integrated RO concept operated as multiple steps under one control panel. All renewable in this design are standard and commercially available at multiple vendors. First the coagulation uses a dosage of 1 kg/m^3 of 40% $FeCl_3$ and produces 3 m^3 of sludge. Secondly the 17 ceramic MF elements (membrane area ≈ 312 m^2) filter out particles and flocs at a flux of 96 LMH. Finally the two RO stages with fluxes of respectively 43 LMH and 13 LMH would require respectively 23 (membrane area ≈ 751 m^2) and 7 (membrane area ≈ 243 m^2) RO elements with a life time of 2.5 years (SWC - Nitto Hydraunautics 360 euro/element). The cost of disposing the coagulation sludge is unknow, and therefore not included in the economic analysis.

Table 24: VSEP/ RO design proposal

design parameter	unit	Value VSEP	Value RO
capacity	m^3/h	30	30
water recovery	%	90	90
Pressure stage 1	bar	34	80
Pressure stage 2	bar	62	120
membrane area	m^2	1825	312 MF 995 RO
number of pack/ elements	#	11	17 MF 30 RO
footprint	m x m	12 x 18	unknown
energy consumption	kw	210	150
chemicals : NLR 303 (2%)	m^3/ week	1.8	1.8

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$FeCl_3$	kg $FeCl_3$ /week		5 000
CAPEX	euro	3 800 000	2 900 000
OPEX[2]: Energy Membrane Chemicals	euro/y	(Total) 600 000 147 000 426 000 351 000	(total) 489 000 6 000 104 000 379 000

DyVaR
The DyVaR system was designed to treat a flow of 7 to 10 m^3/h. The pilot tests showed that a single cyclone evaporates 50L/h. Hence 180 cycles would be installed in Andijk III arranged in six modules of 30 cycles each, for a total capex of 3 100 000 euros. The design is summarized in table 25.

Table 25: VSEP/ RO design proposal

design parameter	unit	Value DyVaR
capacity	m^3/h	7 - 10
water recovery	%	95
number of evaporation cyclones	#	180
footprint	m	8 x 15
energy consumption	kw	1 500
CAPEX	euro	3 100 000
OPEX: Energy Chemicals	euro/y	(Total) 1 054 000 1 000 000 54 000

[2] *OPEX assumes €0.08/kWh and €14.5/gallon membrane cleaners, and FeCl3 is € 95/ton

Summary of feasibility and specific results

This feasibility study was done as part of the DOC2C's project to assess the current technologies for brine treatment and evaluate their possible implementation treating the DOC laden brine arising from the SIX© ion exchange process in WTW Andijk.

In a first part, a number of treatment concepts were assessed using pilot trials to fulfill one on the two brine treatment strategies implementable in Andijk:
1/ The first strategy consists of recovering the NaCl in order to reuse it in the SIX© process, and returning the remaining components to the water source they originate from. This is possible only at the condition that the environmental authorities grant a discharge permit.
2/ If a discharge permit would not be available, the alternative would be the complete treatment of the SIX© brine stream to a ZLD.

ED was selected for the pretreatment of the SIX© brine prior to discharge of the diluate effluent in the water source. This was based on three years of pilot testing, in which it was demonstrated that:

- The technology consistently produced a concentrate of sufficient quality for direct reuse in the SIX© process. The concentrate in fact contains up to 50 g/L of chloride, with minimal contamination of bicarbonate (4,3%), sulphate (2,2%) and DOC (3%).
- The chloride content of the diluate effluent to be returned to Lake IJssel was consistently kept below 1 g/L.
- The lifetime of the ED membranes was found to be feasible. The membranes suffered a limited loss of 30% in exchange capacity over three years.

Implementing ZLD was also technically possible in two steps. The brine would undergo a first volume reduction with RO membranes, then evaporation with the DyVaR technology. To prevent excessive fouling of the RO membranes, two process technologies were compared: the VSEP (implementing vibratory shears during filtration) and an integrated pre-treatment with coagulation and UF filtration prior to ultra-high pressure RO. Both processes achieved similar results with regard to:

- water recovery (up to 90%),
- and permeate quality, which with a TDS content below 1 g/L was found suitable to be returned to the drinking water plant.

Long term operation, which has not been tested as part of this project, should be the determining factor between the two technologies. The DyVaR was selected among various evaporators for its energy efficiency. It demonstrated the ability to produce solid salts and a clear condensate at 98% recovery during pilot testing.

In the second part of the report, design requirements, CAPEX and OPEX for a 30 m^3/h treatment plant in Andijk were evaluated for both strategies. Results showed the implementation of ED technology has a CAPEX of 2,4 millions euros and yearly runs at a cost of 8 000 euros considering the reduction of salt demand in the SIX© process. In contrast, the ZLD option requires an investment between 6 and 6,9 millions euros and OPEX between 1,5 and 1,7 million yearly. The energy requirement is also found to be 5,5 times lower when pre-treating and discharging the SIX© brine than when applying ZLD.
This study showed that out of two technically feasible strategies, the pre-treatment option with ED is the most advantageous both financially and environmentally (based on energy consumption), compared to ZLD. The final decision on the treatment strategy, however, is also dependent on the possible acquisition of a discharge permit from the environmental agencies.

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Cross border and global dissemination

Dissemination of results

Research that is summarized in this feasibility study, along with additional findings that were made during the four-year DOC2C's project have been disseminated in the following ways:

- In each of the four annual workshops, de PWNT gave a presentation to highlight their latest research findings and challenges with DOC and brine treatment. In total, there were 198 attendees to the four workshops. These were a mix of water utility staff and operators, university professors/students, engineers, regulators, and equipment suppliers. It is anticipated that these attendees shared their experiences and newly gained knowledge from the workshops with colleagues where they work/live.
- This feasibility study was presented at the final dissemination workshop, where 48 persons were in attendance.
- This feasibility study is posted on the www.doc2cs.com webpage, for anyone to read or download.
- Presentations made at annual conferences by PWNT staff and students/interns who were also working on this topic while at PWNT. These can be found on the project's webpage.

Incorporation of small-to-medium sized entities (SMEs)

Although the lead partner participated with SMEs in this project, they were not directly related to the brine research herein. (Note that Arvia's brine treatment process was tested in Andijk, but results are reported in 2019 June workshop in Lille – see project webpage).

Technology transfer

Technology transfer is the transfer of a technology from the developer to a third-party user. In this case, the PWN Technologies R&D investigated many technologies for brine treatment for PWN, the water company of North Holland. The R&D efforts will also be applied to other third-party locations, when SIX® or other brine-generating processes are installed at other facilities.

The transfer of technology occurred via:

- Annual workshops networking
- Dissemination workshop networking
- Website posting and information
- Collaboration with project partners and observers/interested parties
- Tours at own facilities to utility staff visitors university visitors, public visitors, engineering visitors, regulatory agency, and manufacturer visitors.
- Working with universities for parts of this research, and introducing this topic to interns from Bath University who worked at PWNT during the DOC2C's years.

Outputs for Project Specific Objective:
Increase technological innovation for DOC removal in drinking water production

No.	Project Outputs	Project Specific Results	Achievements
1	Feasibility studies based on pilot plant operational findings	Widespread dissemination of project research feasibility results to observers, DOC2Cs area, and globally to any interested entity, including less or non-scientific water industry professionals	Achieved (see previous dissemination discussion)
		Increased knowledge base on the applicability of the tested technologies, leading to reduction of overall R&D costs for water treatment	The feasibility study, presentations by PWNT about their study, presentations on the project webpage, together create a knowledge base from which others can learn and start their own evaluation. The R&D efforts and lessons learned of the DOC2C's project help other utilities plan and design for future installations, thereby reducing their potential R&D costs.
		Introduction and consideration of advanced technology applications in areas of low technological performance	Low tech solutions for brine have been disposal to sea or deep well injection. In this feasibility study, the most innovative methods for treatment or separating brine were investigated for brine from the SIX® at PWN. With this experience, new knowledge about how these technologies perform was gained.
		Increased and more rapid introduction of the new technologies where feasible, leading to more efficiencies in water treatment and better water quality	Pilot-testing is a routine way of providing a concept in water treatment. With long-term testing, many seasons of water quality were evaluated and the challenges and waste streams identified. These brines are laden with DOC, because ion exchange is used for DOC removal. Utilities need a solution for brine handling. The R&D efforts of this study can foster a more rapid uptake of brine

			separation, because other utilities have a head-start in their knowledge base by learning about this work.
2	New validated innovative technologies for drinking water treatment developed/designed by partners	Innovative integrated techniques validated on a range of water sources	Brine from PWN and de Water Groep was tested in the DOC2C's project (only PWN brine is discussed in this feasibility study).
		Reliable, future-proof drinking water quality	Not applicable
		Significant reduction (ca. 30%) in formation of disinfection by-products	Not applicable
		Lower ecotoxicity, better public health	Not applicable
		50 to 90% reduction in chemicals use (half or less coagulants dosing and pH conditioning, lower mineralisation)	Not applicable
		Sludge formation reduced at least by half	Not applicable
		Reduction in energy use of various steps	Not applicable
		Desalinated brine as raw material for agricultural purposes	Although not specifically addressed in this feasibility study, agricultural use of desalinated brine was a part of the DOC2Cs project.

Outputs for Project Specific Objective:
Rapid, large scale uptake of technological innovation through cross-border open testing facility

No.	Project Outputs	Project Specific Results	Achievements
3	Innovations from technology providers tested in the pilot facility of the partners	In order to promote the innovative power of technology providers, the partners open their facilities to test new relevant technologies for DOC removal. Tests will range from bench scale to integrated pilot scale. The results are difficult to predict at this stage, but they will aim at:	Different technologies for brine separation were evaluated in this study.
		• Reduced energy consumption	• Not applicable
		• Reduced chemicals use	• Not applicable
		• Reduced by-product formation	• Not applicable
		• Reduced waste	• Not applicable
		• Better water quality	• Not applicable
		This output will also speed up market introduction for new water technologies.	The results of this study can serve as a basis for other utilities to consider brine separation technologies for their current or future water treatment facilities. Having pilot-scale examples of the various systems in use gives confidence and speeds up the implementation by others into the water industry.
4	Water samples from different end-users tested in the pilot facility of the partners	Demonstration of the latest technical innovations on different sources of surface water shall:	Brine from PP3 was tested at LP facility
		• guide other water utilities to adopt the most suitable treatment, leading to rapid transition to high technology and expansion of the adequate infrastructure for water production	• Not applicable
		• speed up market introduction for the new water technologies	• Not applicable