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FEASIBILITY STUDY OF USING ELECTRODIALYSIS TO TREAT AN ANION EXCHANGE BRINE

By

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Bachelor of Science, Environmental Engineering, University of New Hampshire, 2015

THESIS

Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirements for the Degree of

Master of Science
In
Civil Engineering

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This thesis has been examined and approved in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering by:

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Elisabeth Vaudevire, Technological Researcher at PWN Technologies

Dr. Wei Wei Mo, Assistant Professor of Civil and Environmental Engineering

On June 9, 2017

Original approval signatures are on file with the University of New Hampshire Graduate School.
DEDICATION

I would like to dedicate this thesis to the following people:

First of all, to my mother and father for always encouraging me to dream the biggest dreams and teach me the motivation needed to achieve them. I couldn’t have accomplished all of this without your continued support and foundation you raised me on.

And second, to Dr. Malley (BossCAT) for always believing in me and being my role model. You inspired me on my very first day in ENE 400 when you told us your lifetime goal of providing clean drinking water to 1 billion people. You have advised and directed me in a positive direction throughout my undergraduate and graduate studies.
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ABSTRACT

FEASIBILITY STUDY OF USING ELECTRODIALYSIS TO TREAT AN ANION EXCHANGE BRINE

By

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University of New Hampshire, September, 2017

In the drinking water sector, anion exchange technologies are increasingly used for color and disinfection by-products removal, which targets low molecular weight natural organic matter, particularly humic substances (HS). After treatment, resins are regenerated to 99.9% recovery with NaCl resulting in a saline waste stream, referred to as brine. The resulting brine contains left-over NaCl, as well as desorbed inorganic and organic anions (SO$_4^{2-}$, HCO$_3^-$, HS, etc.) from raw water. Disposal of this brine is a problem, especially with regulations becoming increasingly strict. Fortunately, compounds in the brine can be reclaimed if properly separated: NaCl for direct reuse in the regeneration process; and HS as bio-stimulants for crop growth. Previous investigations highlighted the efficiency of using electrodialysis technology to achieve this separation of 1) NaCl with mono-selective membranes and 2) divalent ions from HS with non-selective membranes. However, little was known about the effect of high organic loads from the brine on operations causing fouling or spacer clogging.

The purpose of this research was to evaluate the long-term feasibility of electrodialysis technology for treatment of an anion exchange brine including NaCl and HS recovery. Electrodialysis treatment with mono-selective membranes was evaluated on pilot scale over a six-month period while recording operational data and quality of the by-products. Additional experiments were also conducted to further understand the overall fouling phenomena and lab-
scale simulation of spacer clogging. Results demonstrate that ED treatment with mono- and non-selective membranes is an innovative process, effective at targeting the recovery of resources from concentrated waste streams.
CHAPTER 1

INTRODUCTION

This chapter provides background and context for the research presented in this thesis. A brief history of a drinking water company and its subsidiary (PWN and PWN Technologies, respectively) is summarized. An overview of these companies’ relevant water treatment technologies is also provided. This chapter will also outline the overarching goals of this research, including the purpose of this study, research questions and process design questions.

1.1 PWN Water Company

Puur Water en Natuur (PWN), established in 1920, is the public utility providing drinking water to the province of North Holland, highlighted in Figure 1. PWN owns three major facilities in two locations: Princess Juliana Water Treatment Plant (WTP) and Andijk III in Andijk, and a WTP in Heemskerk. PWN supplies 32 million gallons of drinking water per day (MGD) to individuals, companies, and institutions.

When PWN was established, their main water source was groundwater found in the sand dune area in North Holland, which only required minimal treatment after natural filtration. As the drinking water demand grew, stress on the dunes increased and depleted the groundwater source. Since then, surface water from the Ijssel Lake has replaced groundwater in three ways:

1) Raw water from Ijssel Lake is pretreated at the Princess Juliana facility in Andijk and is artificially infiltrated in the dunes for natural treatment;
2) Some raw surface water is treated through ultrafiltration and reverse osmosis in Heemskerk, then blended with the water from dune filtration; and

3) Water from Ijssel Lake is purified directly in Andijk for local consumption. Recently, this plant was updated with a new pretreatment process referred to as Andijk III WTP, which is the broad context of this thesis.

![Figure 1: Drinking Water Utilities in the Netherlands](image)

Figure 2 summarizes the upgrades of the Andijk WTP throughout its history from 1968 to present. In the most recent upgrade completed in 2014, Suspended Ion eXchange (SIX®) and Ceramic Filtration (CeraMac®) were introduced to replace coagulation, sedimentation, and rapid
sand filtration processes because the end of their useful lives were approaching. The upgraded treatment facility is referred to as “Andijk III WTP”.

Figure 2: Andijk WTP Treatment Process Upgrades

1.2 PWN Technologies

PWN Technologies (PWNT) is a commercial subsidiary of PWN Water Company, which provides innovative solutions in drinking water treatment to water utilities around the world. The Research & Development (R&D) department of PWNT, located on the same site as Andijk III WTP, developed both the SIX® and the CeraMac® technologies. One of the current focuses of the R&D facility is on optimization of the SIX® process and management of the concentrated brine effluents.

1.3 Suspended Ion eXchange (SIX®) Process and Waste Generation

SIX® is an ion exchange (IEX) treatment process which was installed in Andijk for direct treatment of surface water from Ijssel Lake. Its role is to specifically remove the low molecular
weight fraction of natural organic matter (NOM) to avoid fouling on the downstream ceramic membranes and reduce energy and chemical demand in the advanced oxidation process. SIX® uses anion exchange resins for adsorption of charged constituents from the water. On the surface of the resin beads, chloride ions are exchanged for constituents in the water with a higher adsorption rate (Figure 3). Resins are then separated from the treated water and are regenerated with a sodium chloride (NaCl) solution. During this process, the adsorbed NOM is desorbed and chloride is adsorbed back onto the resins, completing the ion exchange cycle. These resins were developed by Laxness for the specific removal of natural organic matter but also have a high affinity towards bicarbonate ($\text{HCO}_3^-$) and sulfate ($\text{SO}_4^{2-}$).

*Figure 3: Resin Desorption of Cl$^-$ and Adsorption of HCO$_3^-$, SO$_4^{2-}$, and NOM*
The sodium chloride solution used for regeneration of the resin is recycled four times before being regarded as a concentrated brine waste (spent regenerant). The concentrate brine now contains a mixture of left over sodium chloride, with desorbed components from the surface water, mainly HCO₃⁻, SO₄²⁻, and NOM. The SIX® process in Andijk generates 25 m³/h of spent regenerant while treating roughly 5000 m³/h raw water from Ijssel Lake.

The exact composition of the spent regeneration brine depends on the parameters of SIX®, such as concentration of NaCl in regeneration solution or how many times the brine is recycled. The SIX® regenerant at the PWNT Pilot Facility contains a higher concentration of NaCl regeneration solution and is recycled six times, whereas the Andijk III SIX® process uses a less-concentrated regeneration solution and recycles regenerant only four times. The composition of each spent IEX Brine is presented in Table 1.

Table 1: IEX Brine Composition

<table>
<thead>
<tr>
<th></th>
<th>Chloride g/L</th>
<th>Bicarbonate g/L</th>
<th>Sodium g/L</th>
<th>NOM mg/L</th>
<th>Sulfate g/L</th>
<th>Nitrate g/L</th>
<th>Conductivity mS/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>IEX Pilot Brine</td>
<td>11</td>
<td>7</td>
<td>15</td>
<td>0.5</td>
<td>7</td>
<td>0.2</td>
<td>45</td>
</tr>
<tr>
<td>IEX Andijk III Brine</td>
<td>5</td>
<td>3</td>
<td>9</td>
<td>0.3</td>
<td>5</td>
<td>0.1</td>
<td>25</td>
</tr>
</tbody>
</table>

1.4 Waste Management: Iron Sludge Vs Spent IEX Regenerant

Before SIX® was installed, softened water was treated with coagulation-flocculation, which generated a ferric sludge. After the transition from coagulation-flocculation to SIX®, the waste stream is changed to a saline brine instead of iron sludge, moving from a solid to liquid waste generation. Therefore, new methods of waste management need to be explored. After consideration of various options, two were retained as most feasible: discharge into the environment (deep well infiltration), or treatment of the waste to achieve zero liquid discharge. If
the saline brine was discharged into the environment, proper permits would need to be issued allowing disposal of concentrated saline brine stream with high-NOM content. While treatment of the saline brine is still in its infancy, it needs more attention to be a feasible option. Previously investigated options include nanofiltration coupled with dynamic vapor decompression and electrodialysis, which focus on salt reuse and byproduct recovery methods (Vaudevire et al 2015). Each of these waste management options involve considerations of costs, sustainability, technical feasibility, and public perception.

Currently, PWN holds a temporary permit allowing the spent SIX® regenerant to be disposed of by deep well injection for the first 4 years of operation until a more sustainable option is fully developed by PWN Technologies. In the meantime, a treatment process based on electrodialysis for the separation and reuse of the brine components is being assessed as a potential long term solution for waste management of the brine generated in Andijk.

1.4.1. Purpose of Brine Treatment

The purpose of treating the brine would be to achieve a complete separation of the main components to reuse them and produce zero waste. Components of interest in the brine are:

- Sodium chloride, which as previously described, is used in SIX® resin regeneration to desorb the anions from the Ijssel Lake water for 99.9% recovery of resins. According to a life-cycle assessment (LCA) study conducted by PWN Technologies, the production of salt (NaCl) used for SIX® regeneration was one of the largest contributors to energy demand (Bogosh et al. 2010). While the regeneration process has been optimized to reduce the amount of salt needed in the process, the excess NaCl in the spent regenerant could be recovered and reused in SIX® resin regeneration.
- **Humic substances** (HS) from NOM have various applications in different industries, such as a biostimulant in agriculture or nutritional supplement in animal food are two of the most common uses of HS. In that regard, when properly conditioned the NOM in the brine could be source of financial revenue.

- **Sodium sulfate** is the third most important byproduct. It finds application either in the glass or paper industries where its recovery from brine rather than produced for this purpose could score favorably on a life cycle analysis. Its value is low but its separation is in anyway necessary for the recovery of NaCl and humic substances.

### 1.4.2. Proposed Solution

The proposed solution in this thesis is to use electrodialysis for the treatment of SIX® regenerant brine to recover and reuse the following constituents: monovalent ions (Cl⁻ and HCO₃⁻); humic substances (NOM); and sulfate ions (remaining multivalent ions).

### 1.4.3. Treatment Mechanisms

Electrodialysis (ED) is a separation technology in which ions are displaced from a diluate to a concentrate solution through ion exchange membranes under the effect of an electrical gradient. Three flow streams are used in ED: diluate, concentrate, and electrolyte. The diluate is the stream that is being “treated”; its conductivity decreases over time. In the case of this thesis, the diluate is the ion exchange brine. The concentrate stream receives the ions, and therefore has a higher concentration of ions and increases in conductivity over time. The electrolyte solution is used to promote the flow of electrons through the use of electrodes; this solution never comes in contact with the diluate or concentrate. The electrolyte solution contains an acid or base and the
following reactions will occur at the cathode (Reaction 1 and 2) and anode (Reactions 3 and 4), respectively (Strathmann 2004, Bernardes et al 2014):

\[
H^+ + 2e^- \rightarrow H_2 \quad \text{(acid environment)} \quad \text{Reaction 1}
\]

\[
H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad \text{(alkaline environment)} \quad \text{Reaction 2}
\]

\[
H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad \text{(acid environment)} \quad \text{Reaction 3}
\]

\[
4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad \text{(alkaline environment)} \quad \text{Reaction 4}
\]

As the electrons are exchanged at the electrodes, there is an electrical gradient which draws ions across the ion-exchange membranes. The acid or base in solution also contributes to the electron exchange, such as sulfamic or sulfuric acid (Strathmann 2004).

Figure 4 displays a cross-sectional view of an ED stack, in which a succession of alternating anion and cation exchange membranes can be seen. Concentrate and diluate flows in between the membranes, also in an alternating manner. Cationic membranes are negatively charged to allow cations to pass across the membrane towards the cathode while retaining anions, whereas anionic membranes are positively charged to allow anions to move towards the anode (Xu 2005, Strathmann 2010). In this setting, the diluate (ion exchange brine) will enter a channel between one anion and one cation exchange membrane. Under the electrical current, the anions will move toward the anode through the anion exchange membrane, and stay in the concentrate channel when encountering the cation exchange membrane. The cations will follow the opposite path though the cation exchange membrane toward the cathode and will also be trapped in concentrate when meeting the anion exchange membrane, assuring the electro neutrality of both streams.
Electrodialysis systems also have different selectivity of membranes: the term mono-selective refers to membranes that allow monovalent ions to pass across the membrane while retaining multivalent ions. The term non-selective is used here to describe membranes that allow monovalent and multivalent ions to pass though. This difference in selectivity will be used in brine treatment to separate the three streams of interest: sodium chloride, humic substances and sodium sulfate. Ion passage with different types of membranes will be discussed further in Chapter 3 and Chapter 4.

The process scheme presented in this thesis for the treatment of the SIX® regenerant brine in Andijk is based on a two-stage electrodialysis process: first a selective separation of monovalent ions (Na⁺, Cl⁻, and HCO₃⁻) from multivalent ions and NOM with mono-selective ion exchange membranes, followed by the separation of sodium sulfate (Na₂SO₄) from the NOMs with standard membranes (non-selective). In the ED process, IEX regenerant brine (i.e. SIX® regenerant brine) will be the diluate, and the ions will be concentrated in the concentrate (reverse osmosis (RO) water). The concentrate from the electrodialysis mono-selective stage will be re-used in the resin
regeneration process. The diluate treated with the mono-selective membranes will continue onto the second stage with standard ED membranes. Sodium sulfate will be concentrated in a new solution of pure RO water, while the NOM will be retained in the diluate. The treated diluate now is a concentrated solution of NOM with low concentration of salts; this can be applied to soils as a biostimulant to improve agricultural growth. Before treating the IEX brine with electrodialysis, the brine is biologically denitrified, therefore nitrate present in the brine will have no effect on the electrodialysis process. However, the brine used in this research was raw regenerant without denitrification.

1.5 Research Description

1.5.1. Research Challenges

Using electrodialysis to treat anion exchange regenerant (IEX brine) proposes a new application of the technology; and no data is publicly available on the performance of the technology overtime. In fact, the high concentration of natural organic matter (NOM) introduces the potential challenge of organic fouling of the ED membranes. Additionally, high NOM values are usually linked to biofouling as an important source of carbon to bacterial development. Finally, the formation of agglomerates and particles when dealing with concentrated salts and organics isn’t excluded which could potentially lead to clogging of the spacers within the stacks.

During initial testing of the pilot system showed particularly good ionic compound separation for mono selective membranes. However polymeric based materials such as the ion exchange membranes oftentimes lose their original properties under the effect of regular cleanings, time, or fouling. This ageing phenomena has been described in other applications but is believed to be directly linked to the quality of the diluate. These parameters are unknown for the treatment of anion exchange regenerant.
1.5.2. Research Objectives

The purpose of this thesis is to complete a feasibility study on the long-term use of electrodialysis (ED) to treat spent regeneration (Suspended Ion Exchange, SIX®) brine at PWN Technologies (PWNT) with respect to the fouling and aging of ED membranes. The study is conducted on pilot scale to follow the evolution of operational parameters and draw conclusions of the fouling and/or ageing rates of the membranes. However, it is also well known that most parameters are interrelated which can make the interpretation with regards to fouling and ageing difficult. Therefore, this work has included bench scale targeted experiments designed to isolate and understand specific phenomenon such as:

- Spacer clogging, investigated on a bench scale spacer cell
- Biofouling potential, investigated through microbiological regrowth tests
- Ageing, or state of the membranes, investigated by physical burst tests and membrane resistance etc.

Overall the project has four main objectives:

1. Monitor operational parameters related to fouling over time: ion passage, speed of ion transfer, current density, conductivity, and quality of the concentrate at 90 mS/cm;
2. Measure the impact of performing electrodialysis reversal (EDR), where flows and polarity of the stack are reversed, on operational parameters mentioned above, and define an optimum frequency;
3. Observe and measure the level of spacer clogging over time with respect to pressure increase and particle concentration in the influent and effluent;
4. Assess the feasibility of further treating the chloride-free ED diluate using non-selective membranes for the separation of remaining inorganics from organics.
1.5.2.1. Monitoring operational parameters related to fouling over time

While physical fouling inhibits the performance of electrodialysis membranes, PWNT is also interested in the ageing of ED membranes with respect to mono- and multi-valent ion passage across the ED membranes (ion selectivity). This is an important parameter to address because the recovered sodium chloride solution will be used for IEX resin regeneration. If the concentrate is contaminated with a significant amount of sulfate and/or NOM (multi-valent ions), the IEX resins may not be regenerated to their full capacity because they have a higher affinity to the multivalent ions compared to chloride. Therefore, the first research objective is to quantify the amount of sulfate and NOM contamination of the concentrate, and how much ion selectivity decreases over time, if at all.

Research questions relevant to multivalent ion passage across ED membranes:

1. What is the concentration of sulfate and NOM in the sodium chloride recovery stream (concentrate)?
2. Does ion selectivity change over time?
3. Does the frequency of EDR impact ion selectivity over time?

1.5.2.2. Impact of Electrodialysis Reversal and Cleaning in Place

Fouling of electrodialysis membranes is inevitable with SIX® brine due to the high NOM concentration. Fouling is due to deposition or adsorption of material from the brine caused by particulates, biofouling, organic fouling, and/or scaling. Details and consequences of these foulants are discussed in Section 2.2. There are two ways to restore the performance after the membranes have been fouled: electrodialysis reversal (EDR) and a chemical cleaning in place (CIP).

This research was aimed at determining the amount of fouling that occurs over time on the ED membranes with respect to membrane performance and the efficiency of frequent EDRs and
CIPs. Current density and conductivity are measured at the pilot scale to determine membrane performance. Other research objectives are to assess the impact of different EDR frequencies (how often the pilot system is reversed) and of using a preventative cleaning in place (scheduled CIPs). Ultimately, this analysis will be used to determine the optimal reversal time at full-scale.

Research questions related to the impact of EDR and preventative cleaning include:

1. How often do fouling events occur and can the causes be identified?
2. What are optimum frequencies for electrodialysis reversal and CIP?
3. What is the best procedure for reversal (classic or flash)?
4. Do CIP or membrane ageing have a negative impact on membrane selectivity?

1.5.2.3 Spacer Fouling Over Time

In the electrodialysis stack, membranes are separated with spacers, similar to reverse osmosis (RO) spacers, such that they are composed of a lattice structure to direct the flow between membranes. The difference between RO and ED spacers is the ED spacer has a finer lattice. Therefore, suspended particles in the IEX brine can clog the spacer, which may result in operational challenges due to pressure increases and flow decreases.

The objective is to determine the level of spacer clogging due to particulates using a bench-scale spacer unit, sized for one membrane and spacer pair. This was done by using a systematic approach to recreate the same conditions in the pilot ED stack by changing one parameter at a time. The aim of this objective is to assess the impact of spacer size and influent brine quality on spacer fouling, while comparing the pressure increase at the head of the spacer unit to that of the ED stack.

Research questions relevant to spacer fouling with respect to suspended material:
1. Can particle fouling and its effect on pressure increase be observed in the cell unit? If so, does the size of spacer have an impact?

2. Can pretreatment help reduce particle fouling? If so, how much pretreatment is required?

1.5.2.4. Feasibility of Further Treating Chloride-Free Diluate

After the IEX brine is treated with mon-selective membranes to remove monovalent ions (chloride, bicarbonate), the diluate contains a high concentration of NOM and sulfate. NOM and sulfate need to be separated in order for the NOM to be reused in agricultural applications; NOM can be reclaimed as a biostimulant and sulfate can be reclaimed for the glass or paper industry.

Therefore, the objectives are to determine the degree of separation and to improve the separation of NOM and sulfate. Two experiments were conducted. The first experiment used chloride-free brine to determine the maximum conductivity for the concentrate, while measuring the NOM and sulfate concentrations as conductivity increased over time. The second experiment adjusted the acidity of the chloride-free diluate to determine if sulfate separation could be improved.

Research questions relevant to spacer fouling with respect to suspended material:

1. Is complete separation of sulfate from NOM possible for the chloride-free diluate?

2. At what point is the maximum conductivity reached in the sulfate concentrate?

3. Will adjusting the pH of the chloride-free diluate improve separation of sulfate from NOM?
CHAPTER 2

LITERATURE REVIEW

This chapter will include a synthesis of the existing knowledge and technology of electrodialysis (ED) with emphasis on electrochemical and mechanical properties, as well as fouling and ageing of ED membranes. This chapter also discusses data previously collected on ED treatment of anion exchange brine at PWNT, which provides valuable insight to bench-scale applicability of this technology to treat an anion exchange brine with high-NOM concentration.

2.1 Electrodialysis Theory

2.1.1 Structure of Ion-Exchange Membranes

Ion exchange membranes used in electrodialysis are developed using a polymer matrix, which contain fixed cationic or anionic groups resulting in two types of electrically conductive membranes: cationic and anionic membranes. Cationic membranes are introduced to a strong or weak acid for a fixed negative charge (sulfonic or carboxylic acid), whereas anionic membranes are introduced to a strong or weak base for a fixed positive charge (quaternary or tertiary amines) (Strathmann 2010, Valero et al 2011, Bernardes et al 2014). Counter- and co-ions are also present in the polymer matrix, both of which are mobile. The counter-ions determine the charge of the polymer matrix. Fixed ions are in electrical equilibrium with mobile counter-ions in between the polymer, however, the mobile co-ions are essentially excluded from the polymer matrix because their charge is identical to the fixed ion (Naragale et al 2006). Figure 5 illustrates a schematic
drawing of the structure of a cation exchange membrane with anionic fixed-ions, cationic counter-ions, and anionic co-ions. Similarly, anionic membranes have anionic counter-ions and cationic co-ions (not shown in Figure 5) (Strathmann 2010).

Figure 5: Schematic Drawing Illustrating Ion-Exchange Membranes

(a) a cation-exchange membrane with a homogeneous structure and (b) an ion-exchange membrane with a heterogeneous structure prepared from an ion-exchange resin powder and binder polymer (Strathmann 2010)

Ion exchange membranes can also be characterized based on the preparation of the membrane; homogeneous or heterogeneous. Homogenous membranes are prepared by introducing the fixed-ion directly into polymer matrix, which results in an evenly distributed charge (negative or positive) on the membrane. Heterogeneous membranes combine a fine ion-exchange resin powder with a binder polymer, resulting in an uneven distribution of ion-exchange sites in the polymer matrix. Comparatively, homogeneous membranes have better electrochemical properties whiling lacking in mechanical properties, whereas heterogeneous membranes have better
mechanical properties while lacking in electrochemical properties. (Strathmann 2010, Sata 2007, Naragale et al 2006).

2.1.2. Ion-Exchange Membrane Properties

Important ion exchange membrane characteristics are broken into two categories: electrochemical and mechanical. Electrochemical properties of ion exchange membranes include permselectivity, electrical resistance, and ion exchange capacity. Mechanical properties of ion exchange membranes include membrane thickness, swelling, dimensional stability, tensile strength, and hydraulic permeability.

2.1.2.1. Electrochemical Properties

*Permselectivity*, or ion-selectivity, of ion exchange membranes refers to the ability to transport ions of the same charge as counter-ions and inhibit migration of those with the same charge as the co-ions across the membrane. For instance, a cationic membrane will have a higher permselectivity to cations and anions will be retained explained by the Donnan exclusion theory (Donnan 1924, Tanaka 2010). Permselectivity is dependent on the concentration of electrolytes in solution, concentration of fixed-ions, valance of co-ions, valance of counter-ions, and the affinity of the exchanger with respect to the counter-ions (Nagarale et al 2006). Ideally, the ion exchange membranes should have high permeability (or transport) of counter-ions and no permeability of co-ions (Bernardes et al 2014).

Concentration of the electrolyte affects ion-selectivity of ion exchange membranes due to the membrane potential. Membrane potential is the electrical potential between two solutions of different ionic concentrations. Without applying electricity, ions will naturally move from the
high-concentrated solution across a selective membrane (cationic or anionic) into the low-concentrated solution to reach equilibrium. Due to the selectivity of the ion exchange membrane, the membrane will reject ions of the same charge of the co-ion, therefore creating the electrical potential between the two solutions (Sata 2007, Tanaka 2010). Permselectivity is the highest when there is a low-concentration of the target ion on the opposite side of the membrane and is decreased as ions move across the membrane due to the decreasing concentration gradient.

The concentration of fixed ions effects the permselectivity, where a higher amount of fixed ions within the polymer matrix increases permselectivity due to a greater number of ion exchange sites, increasing the flow of ions across the membrane. Depending on permselectivity and ion exchange capacity, membranes can either be mono-selective (transport of monovalent ions only) or non-selective (transport of mono- and multi-valent ions). The valance of ions in the polymer matrix and membrane affinity also plays a role in permselectivity. As valance, or electronegativity, of the ions increases, there is a greater force of attraction between the ions which indicates that a higher valance for the counter-ions will have a stronger attraction to the ion exchanger. Membrane affinity relates in a similar way such that the ions will be more selective to certain ions over others. For example, if a membrane has a high affinity toward chloride ions (Cl\(^-\)) and a low affinity towards bicarbonate (HCO\(_3^-\)), the membrane will be more permeable to Cl\(^-\) as opposed to HCO\(_3^-\). This is referred to as preferential permselectivity, which can be calculated using Eq. 1, where \(S_B^A\) is the selectivity of ion A with respect to ion B, \(m_A(0)\) is the initial mass of ion A, \(m_A(t)\) is the final mass of ion A, \(m_B(0)\) is the initial mass of ion B, and \(m_B(t)\) is the final mass of ion B (Zhang et al 2010):
\[ S_B^A = \frac{\left( \frac{m_A(t)}{m_A(0)} \right) \left( \frac{m_B(t)}{m_B(0)} \right) \left( 1 - \frac{m_A(0)}{m_A(t)} \right) + \left( 1 - \frac{m_B(0)}{m_B(t)} \right) \left( 1 - \frac{m_A(t)}{m_A(0)} \right)}{\left( \frac{m_A(0)}{m_A(t)} \right) + \left( 1 - \frac{m_B(0)}{m_B(t)} \right)} \] (2)

Selectivity ranges from 0 to 100%; 0% selectivity indicates that the membrane selectivity of ion A is identical to that of ion B, while 100% selectivity indicates that the membrane is completely preferential to ion A. For example, mono-selective membranes are selective towards monovalent ions. Therefore, if a solution with chloride ions, NOM, and sulfate ions is being treated with mono-selective membranes, the selectivity of chloride ions to NOM or sulfate should be close to 100%.

Another method of measuring permselectivity is by using the transport number of ions which is presented as the percentage of current carried by the exchanger ions through the membrane in relation to the total current carried through the membrane (Naragale et al 2006, Strathmann 2010). In electrodialysis, current efficiency is used to determine the transport capabilities of the membrane. Current efficiency essentially quantifies the membrane’s capability of transporting ions (Eq. 3), where \( z \) is the charge of the ions, \( F \) is the Faraday constant, \( V_{od} \) and \( V_{fd} \) are the volume at the beginning and end of the experiment, \( C_{od} \) and \( C_{fd} \) are the concentrations of ions at the beginning and end of the experiment, \( n \) is the number of membrane cell pairs, \( I \) is the current applied, and \( \Delta t \) is the duration of the experiment (Sata 2007).

\[ \text{Current Efficiency} \ (\%) = \frac{zF \times (V_{od}C_{od} - V_{fd}C_{fd})}{nI \times \Delta t} \times 100\% \] (4)

Electrical resistance is the ease at which ions are transported across the membrane dictating the energy required to achieve a desired demineralization (Kneiefel et al 1980, Naragale et al 2006, Bernardes et al 2014). Electrical resistance is determined by using the slope of the current-voltage curves and is typically measured in (Ω-cm), or as membrane area resistance (Ω-
cm\(^2\)) (Naragale et al 2006). The electrical concentration gradient effects electrical resistance; there will be less electrical resistance with a large electrical gradient where ions are moving from the high- to low-concentration, whereas electrical resistance increases as the electrical gradients shifts.

This concept can be observed with the measure of current density, where current density is the amount of ionic flow across the membrane per membrane area. A decrease of current density is a consequence of an increase of electrical resistance. When the concentration of permeable ions reaches zero, limiting current density has been reached (Strathmann 2010). Figure 6 is a typical current-voltage curve to determine the limiting current density. In the first zone of Figure 6, current density linearly increases with increasing voltage. Here, the current density is not limited and resistance is calculated using Ohm’s law (Eq. 5), where I is current (Amps), V is voltage (volts), and R is the resistance (ohms, \(\Omega\)):

\[
I = \frac{V}{R}
\]

The limiting current density is identified at the intersection of the first and second zones, where ion depletion occurs at the membrane surface and limits the current. The third zone is the overlimiting current zone which could be due to water dissociation, exaltation of ions, gravitational convection, or electro-convection (Strathmann 2010, Bernarida et al 2014).
Ion exchange capacity (IEC) of the polymer matrix quantifies the ion exchange transfer based on the amount of fixed- and counter-ions. ICE directly affects permselectivity and electrical resistance. Permselectivity is impacted by IEC such that the concentration of counter-ions (ion exchange groups) in the polymer matrix either increases or decreases the exchange capability; high concentration of counter-ions increases permselectivity, whereas low concentration decreases permselectivity. While the concentration of the ion exchange groups is important, the type of exchange groups used is also important (Naragale et al 2006, Bernardes et al 2014, Kneifel et al 1980). IEC also impacts electrical resistance such that electrical resistance decreases with decreasing concentration of ion exchange groups.

Two more concepts that are important to consider when discussing electrochemical properties are osmosis and electro-osmosis. Osmosis is the diffusion of constituents suspended in a solvent over a semi-permeable membrane due to a chemical potential. In electrodialysis, ions migrate from the dilute into the concentrate due to the electrical current caused by the anode,
cathode, and electrolyte (Sata 2007). Osmotic pressure increases as the concentration of ions in the diluate decrease and concentrate increases in the concentrate. The increase of osmotic pressure also increases the electrical resistance across the membrane, therefore increasing the amount of energy required to transfer ions. When electricity is applied to the electrodialysis system, water molecules transfer the ions across the membrane due to electro-osmosis. Water transport ($W_o$, (mole•s$^{-1}$)) due to osmosis is calculated using Eq. 7, where $K_o$ is osmotic water transport constant (L•s$^{-1}$•m$^{-2}$), $\Delta \Pi$ is difference in osmotic pressure (bar), $n$ is number of cell pairs, and $A$ is membrane area (m$^2$) (Pronk et al 2006).

$$W_o = K_o \Delta \Pi n A$$  \hspace{1cm} (8)

Osmotic pressure is calculated using Eq. 9, where $R$ is the gas constant (8.3144 J•mol$^{-1}$•K$^{-1}$), $T$ is temperature (K), $k$ is an empirical osmotic transport factor, and $\chi$ is electrical conductivity (mS/cm). Therefore, water transport due to osmosis is expressed in Eq. 10 (Pronk et al 2006) As osmotic pressure increases, more water will pass across the membrane per ion transferred (Tanaka 2010).

$$\Delta \Pi = RTk \Delta \chi$$  \hspace{1cm} (11)

$$W_o = K_o RTk \Delta \chi n A$$  \hspace{1cm} (12)

Electro-osmosis states that the ions dissolved in water will also draw water molecules across the membrane because ions are surrounded with polar molecules of water due to their charges. Water transport due to electro-osmosis ($W_E$) is calculated using Eq. 13, where $k_E$ is the electro-osmotic water transport constant (mole/val), $CE$ is current efficiency, $n$ is the number of cell pairs, $I$ is the electric current (A), and $F$ is Faraday’s constant (Pronk et al 2006).

$$W_E = k_E \frac{\gamma}{\Delta t} = k_E CE n \frac{I}{F}$$  \hspace{1cm} (14)
Total water transport \((W_T)\) can then be calculated with Eq. 15.

\[
W_T = W_E + W_o = k_E C E n \frac{I}{P} + k_o \Delta \chi n A
\]  

(16)

Factors that affect water transport include surface-charge density, hydration enthalpy of the cations exchanged in the membranes, and water content of the membrane (Xi et al 1995).

2.1.2.2. Mechanical Properties

Tensile strength is a measure of the rigidity of the membrane; how durable the membrane is. The membrane polymer matrix impacts the tensile strength because the more crosslinking of the polymers (higher density of polymer network), the tighter the matrix and therefore a stronger material is formed (Strathmann 2010, Naragale et al 2006). Tensile strength is measured at \(\text{kg/mm}^2\), or can also be expressed as burst strength which has the units of MPa (Sata 2007).

Hydraulic permeability is a measurement which observes transport of components due to hydrostatic pressure. Hydrostatic pressure should not allow passage of components across the membranes, therefore hydraulic permeability defines any passage of ions or water due to physical pressure applied. Water transport might be seen if there are any physical damages to the membrane, such as pinholes in the membrane. In this case, the hydraulic permeability test would yield invalid results since water is passing over the membrane due to physical damage rather than chemical or mechanical damage (Nagarale et al 2006, Sata 2007). Hydraulic permeability (Eq. 17) is expressed as:

\[
\frac{\Delta mL}{[(h)(m^2)(0.1 \text{ MPa})]}
\]

Additional mechanical properties include membrane thickness, swelling, and dimensional stability. Membrane thickness usually increases electrical resistance of ion exchange membranes therefore, thicker membranes have decreased ion flux across the membrane (Sata 2007). Similarly,
membrane swelling decreases ion exchange performance due to increasing the electrical resistance. Typically, membrane swelling is caused by osmotic pressure of water (Ghallousi et al 2013). Membrane swelling will negatively impact permselectivity, electrical resistance, and hydraulic permeability (Bernardes et al 2014). Finally, the dimensional stability of the membrane relates to the membrane’s durability to temperature increase with respect to preserving mechanical and electrochemical characteristics. Thermal stability of membranes varies depending on the polymer matrix; anionic membrane introduced to quaternary ammonium groups are durable up to 80°C and 120°C for cationic membrane with sulfonic acid groups) (Sata 2007).

To summarize, there are tradeoffs when selecting ion exchange membranes for electrodialysis processes with respect to ideal characteristics: high permselectivity, low electrical resistance, good mechanical strength and stability, and good chemical stability (Strathmann 2010). Permselectivity, electrical resistance, and IEC impact the flow of ions across the membrane due to the structure of the polymer matrix. High crosslinking of the polymer matrix leads to increased mechanical properties, decreased permselectivity, and increased electrical resistance. High concentration of ion exchange groups increases ion exchange capability and permselectivity, while decreasing electrical resistance and mechanical properties (Sata 2007, Strathmann 2010, Naragale et al 2006).

**2.2 Fouling and Ageing of Ion-Exchange Membranes**

This section expands on the causes, consequences, and potential remedies of membrane fouling and ageing.

2.2.1. **Fouling of Ion Exchange Membranes**

The semi-permeable and conductive nature of electrodialysis membranes introduces a significant challenge of fouling and degradation of ion exchange membranes. There are two
fouling extremes: reversible and irreversible fouling; and four types of membrane fouling: colloidal fouling, organic fouling, scaling, and biofouling. Over time, the membranes naturally begin to age which involves the decomposition of the membrane, such as reduction in thermal or chemical stability. Fouling and ageing of ion exchange membranes decreases permselectivity, while increasing electrical resistance and membrane damages (Mikhaylin et al 2016).

Fouling is caused by the selective nature of the polymer matrix; higher molecule weight which prevents ion migration into the concentrate as a result of high density of crosslinking in the polymer matrix (Korngold et al 1978, Strathmann 2010). Salt precipitation forms on the surface of the membrane or in the polymer matrix, resulting in membrane fouling or poisoning (deposition in the membrane matrix, rather than on the surface of the membrane) (Bernardes et al 2014, Ghalloussi et al 2013, Sata 2007, Choi et al 2003). Typically, organic fouling occurs on the anionic exchange membrane, and inorganic fouling (scaling) occurs on the cation exchange membrane due to the common charge of the foulant (Lindstrand et al 2000, Ghalloussi et al 2013).

2.2.1.1. **Colloidal Fouling**

Colloidal fouling refers to the attachment of charged particles on the membrane surface such as clay minerals, colloidal silica, iron oxide, aluminum oxide, manganese oxide, organic colloids, etc. Figure 7 shows the typical charge composition of a colloidal particle, where the innermost layer has a strong positive charge which attracts and adsorbs negatively charged matter in solution (Stern layer). The outer most layer is the diffusion layer, which neutralizes the “excessive” charge on the particle and prevents it from coagulating with other particles (Mikhaylin et al 2016). The resulting colloid has a net charge; commonly colloids in water treatment solutions is negatively charged. Negatively charged particles are a challenge for anion exchange membranes since they are too large to pass through the membrane but are attracted towards the positively
charge ion exchange groups. Therefore, this ion exchange site is blocked by the colloid preventing permeable ions to pass through.

![Model of Positively Charged Colloidal Particle](image)

*Figure 7: Model of Positively Charged Colloidal Particle (Mikhaylin et al 2016)*

### 2.2.1.2. Organic Fouling

Unlike colloidal fouling, organic fouling is caused by dissolved organic matter, such as oil, carbohydrates, proteins, aromatic substances, and humic acids. The charged organic substances adsorb onto the surface of the ion exchange membrane or get stuck in the membrane channel due to electrostatic or hydrophobic interactions (Mikhaylin et al 2016). Organic fouling on ion exchange membranes is impacted by the size and charge of dissolved organic matter, such that membranes will have a lower permselectivity towards ions of higher molecular weight. For example, natural organic matter (NOM), a common constituent in many drinking water sources, has a relatively large molecular weight with a negative charge. Therefore, NOM is attracted to the anion exchange membrane but is nearly impermeable due to its size, especially in mono-selective membranes (Korngold et al 1978, Kim et al 2002). NOM is negatively charged, which suggests the anion exchange membrane will be more prone to organic fouling. NOM adsorption is decreased with increasing ionic strength and decreasing pH due to changes induced in the NOM and the
competition with permeable ions in solution. The electronegativity and molecular size of NOM is decreased when there are more H\(^+\) ions in solution because NOM will “coil” up on itself reducing its overall wetted hydraulic radius. Additionally, Kim et al 2003 studied the influence of acidic conditions of NOM fouling, and found that NOM fouling was approximately three time greater in higher pH solutions than lower. In the application of mono-selective membranes treating a solution with a high concentration of chloride ions and NOM present in solution, the membranes will have a higher affinity towards the chloride (Kim et al 2002, Zhang et al 2010). However, when the concentration of chloride ions is lower than that of the NOM, the potential of organic fouling will increase.

In the application of standard, or non-selective, membranes, ion selectivity is not as restrictive, and therefore there is a higher potential for NOM to pass through the membrane. However, NOM still hinders salt passage, such as sulfate, because NOM will be transported through the membrane at a slower rate or fouling the surface of the membrane if its molecular size is too large (Lindstrand et al 2000).

2.2.1.3. Scaling

Scaling of ion exchange membranes is a result of precipitation of salt (typically Ca(OH)\(_2\), Mg(OH)\(_2\), CaCO\(_3\), MgCO\(_3\), CaSO\(_4\)) on the membrane surface (fouling) or within the polymer network (poisoning) (Korngold et al 1970). Three factors impact scaling of ion exchange membranes: temperature, concentration of ions, and pH. As the solution becomes more basic, two reactions occur that will increase potential membrane scaling: hydroxide (OH\(^-\)) either precipitate out with Ca\(^{2+}\) or Mg\(^{2+}\) (Reactions 5 and 6), or reacts with bicarbonate resulting in a higher concentration of carbonate (CO\(_3^{2-}\)) (Reactions 7 and 8) (Figure 8).
While solution characteristics play a significant role in membrane scaling, the composition of the polymer matrix also effects the potential of scaling, such as its permselectivity (Mikhaylin et al 2016). Mono-selective membranes, selective to mono-valent ions only, have low permeability of multivalent ions. As a result, the concentration of multivalent ions (Ca$^{2+}$, Mg$^{2+}$, SO$_4^{2-}$) increases in the diluate, which also increases the potential of scaling on the ion exchange membrane. Scaling typically occurs at the cation exchange membranes when the pH is basic, whereas scaling occurs on the anion exchange membrane at neutral pH (Korngold et al 1970, Mikhaylin et al 2016).


2.2.1.4. **Biofouling**

Biofouling of ion exchange membranes is a result of microorganisms and organic matter building up on the surface of the membrane eventually leading to biofilm formation. Microorganisms are typically negatively charged therefore, it is more likely biofouling will occur on the anion exchange membrane opposed to the cation exchange membrane (Maddah et al 2016). Biofouling is dependent on the concentration of microorganisms, assimilable organic matter, and colloidal particles. When those three components are present in solution, temperature is also a factor; biofouling is more likely to occur at higher temperatures (35°C) versus lower temperatures (18°C) because microbial growth rates double for every 10°C increase (Maddah et al 2016). In the electrodialysis system, temperatures between 15-25°C is observed depending on the amount of power required to transport ions. Temperature increases as ion concentration decreases due to the higher amount of power required. There are three major steps of biofilm formation: attachment, growth, and dispersal (Figure 9). The first stage of “attachment” is broken down into two sub-stages: initial interaction between biological matter and membrane, and adhesion to the membrane surface. Attachment can be reversed by rinsing the membranes with chemicals however, if ignored the biomass will continue to grow and will become irreversible, requiring the membranes to be replaced (Mikhaylin et al 2016).
Biofouling potential can be estimated by measuring the biomass production potential (BPP) and assimilable organic carbon (AOC) for the solution of interest. The BPP experiment measures the maximum concentration of adenosine triphosphate (ATP) of naturally occurring microorganisms in a sample incubated at 25°C. The AOC analysis applies two strains of microorganisms (*Pseudomonas fluorescens* (P17) and *Spirillum* sp. strain (NOX)) which are proven to utilize organic compounds and acids, respectively, to measure the maximum colony counts in a sample incubated at 1°C (Vrouwenvelder et al 2000). These two experiments will provide an estimate of the level of nutrients available for microorganism to reproduce, as well as the quantity of microorganisms already present in the solution.

### 2.2.2. Ageing of Ion Exchange Membranes

Ageing of electrodialysis membranes occurs over a long period of time as the membrane becomes irreversibly fouled or poisoning, as discussed in the literature above (Ghalloussi et al 2013). Scaling, organic fouling, colloidal fouling, and biofouling of ion exchange membranes can permanently damage (decompose or deteriorate) the ion exchange groups in the polymer matrix.
This results in a reduction of ion exchange capacity and/or permselectivity, and therefore increases electrical resistance (Ghalloussi et al 2013).

2.2.3. Identification of Membrane Fouling and Ageing

The most common way to identify membrane fouling, poisoning, or ageing is to measure the electrochemical and mechanical properties of the used membrane and compare the results to new membranes. Electrical resistance, ion exchange capacity, permselectivity, hydraulic permeability, and tensile strength are typically measured to assess the current state of the membranes. Unfortunately, some of these methods are invasive, such that membranes need to be physically removed from the stack to inspect the quality and performance. However, a non-invasive technique includes measuring current density as a rough estimate of the state of the ion exchange membranes. Figure 6 illustrates the Current-Voltage curve, where voltage is varying. This figure states that the current is proportional to voltage increases until the limiting current, and research suggests the limiting current should not be exceeded. Therefore, if current density is measured at a constant voltage, fouling can be identified when current density continues to decrease over time under the same conditions (Zhang et al 2010, Ghalloussi et al 2013, Khan et al 2016).

Other measures of fouling could be through measuring the ion selectivity of the membranes because as membranes foul or age, permselectivity is decreased due to a decrease in ion exchange capacity. Therefore, if permselectivity (ion selectivity) decreases, membrane performance has decreased (Ghalloussi et al 2013).
2.2.4. Control and Prevention of Membrane Fouling

There are four common strategies of controlling and preventing membrane fouling: pretreatment to remove or reduce foulants, membrane modification, electrodialysis reversal, or chemical cleaning in place. This thesis will only focus on electrodialysis reversal and chemical cleaning.

2.2.4.1. Electrodialysis Reversal

Electrodialysis reversal (EDR) is alteration of the electrodialysis process, where the technology has additional functionalities, such as ability to reverse polarity and flow through the membranes. EDR significantly reduces fouling potential by reversing the anode and cathode as shown in Figure 10. Fouling occurred on the surface of a mono-selective membrane due to impermeable, negatively charged matter (e.g. NOM or SO$_4^{2-}$) in solution. The polarity of flow streams is reversed – the cathode is now the anode and vice versa, while the diluate is not the concentrate and vice versa. The system reversal now allows the negatively charged material to detach from the anion exchange membrane and migrate towards the opposite side. This reversal is similar to a filter backwash however, the membranes are fully functional during most of the EDR, except the few minutes during the flushing process. EDR has been proven to significantly reduce the amount of irreversible fouling (Strathmann 2010, Katz 1979, Mikhaylin et al 2016, Fubao 1985, Allison 1995). The frequency at which the system is reversed depends on the characteristics of the diluate and ion exchange membranes being used. EDRs can occur every few minutes to hours.
An alternative EDR method is called “pulse electric field,” which involves only reversing the electrodes therefore increasing current density across the membranes. This method has been proven to reduce fouling caused by natural organic matter and concentration polarization sending a surge of power in the opposite direction allowing the deposited material to detach from the membrane and migrate towards the opposite membrane (Lee et al. 2002).

### 2.2.4.2. Chemical Cleaning in Place

Chemical cleaning in place (CIP) is proven to remove or reduce reversible fouling on the membranes. The type of chemical required depends on the type of fouling that has occurred. Table 2 presents a variety of cleaning agents for each fouling type. For example, a common cleaning agent for organic (humate) fouling is an alkali solution, and a common cleaning agent for scaling is hydrochloric acid.
Table 2: Cleaning Agents for Different Types of Membrane Fouling (Mikhaylin et al 2016)

<table>
<thead>
<tr>
<th>Fouling type</th>
<th>Examples</th>
<th>Cleaning agents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colloidal</td>
<td>SiO$_2$, Fe(OH)$_3$, Al(OH)$_3$, etc.</td>
<td>Chlorination, alkali rinsing, anticoagulants and dispersants</td>
</tr>
<tr>
<td>Organic</td>
<td>Polysaccharides, proteins, peptides, fatty acids, humate, surfactants</td>
<td>Alkali rinsing salt solutions, isopropanol</td>
</tr>
<tr>
<td>Scaling</td>
<td>CaCO$_3$, Ca(OH)$_2$, Mg(OH)$_2$, CaSO$_4$, etc.</td>
<td>Citric acid, EDTA, hydrochloric acid, antiscalants</td>
</tr>
<tr>
<td>Biofouling</td>
<td>Bacteria, biofilms, transparent exopolymer particles, etc.</td>
<td>Enzymes, surface active substances, chaotropic agents, biocides, nitric oxide, etc.</td>
</tr>
</tbody>
</table>

While cleaning with chemical agents may restore membrane performance with respect to removing or reducing fouling, frequent cleaning may increase the rate of membrane ageing with respect to the electrochemical and mechanical properties, specifically the degradation of ion exchange groups and the polymer matrix (Mikhaylin et al 2016, Garcia-Vasquez et al 2014, Bauer et al 1990).

To determine if the CIP was effective, a demineralization test can be conducted to measure the effectiveness of the cleaning. A desalination rate is calculated using Eq. (19), where $R_w$ is the desalination rate (%), $\delta_0$ is the initial conductivity of the diluate (mS/cm), and $\delta_t$ is the final diluate conductivity at the end of the experiment (mS/cm) (Khan et al 2016):

$$R_w = \frac{\delta_0 - \delta_t}{\delta_t} \times 100$$

(20)

If membrane performance is restored, the desalination rate will stay roughly the same over time. However, with irreversible membrane fouling or membrane degradation (or ageing), the desalination rate will decrease which suggests there is less ion migration from the diluate to the concentrate over time.

2.3 Prior Electrodialysis Research at PWNT

2.3.1. Bench-Scale Study on Ion Separation of IEX Brine

A bench-scale study was conducted to assess the impact of the current, flow rate and brine composition on the separation of sodium chloride, sulfate, and natural organic matter through two
electrodialysis stacks containing mono-selective and non-selective membranes. This study is important because it provides preliminary data on the passage of ions through ED membranes before scaling up the research to pilot-scale. This section is a summary of the study presented in Bonneau et al. 2014. Additional information is provided in Appendix D.

PCCell ED 64002 cell unit was used in conjunction with a pump unit and ED membranes. PCCell 64002 cell unit contains ten cell pairs of anionic and cationic membranes, and the pump unit contains a flow path for each ED stream: electrolyte, concentrate, and diluate. At no point do the flow paths come in contact with each other. Figure 11 illustrates the schematic of PCCell ED 64002 cell and pump units with each respective flow path.

The mono-selective experiments with the PCCell ED 64002 cell unit was operated at different current densities (56, 103, and 164 A/m²) while the voltage was varied until it reached the maximum voltage of 20 V. The cell unit was run until the conductivity was below 0.7 mS/cm for the synthetic brine and 17-18 mS/cm (80-90% Cl⁻ transfer) for the PWNT IEX brine. The diluate which was treated with the mono-selective membranes was saved and then treated with the non-selective membranes. The non-selective experiments with the PCCell ED 64002 cell unit was operated at different current densities (41, 56, and 103 A/m²) while the voltage was varied until it reached the maximum voltage of 20 V.
Figure 11: Schematic of PCCell ED 64002 Cell Unit (Bonneau et al 2014)

Table 3: Diluate characteristics (Bonneau et al 2014)

<table>
<thead>
<tr>
<th>Brine</th>
<th>[Cl\textsuperscript{-}] (g/L)</th>
<th>[SO\textsubscript{4}\textsuperscript{2-}] (g/L)</th>
<th>[HCO\textsubscript{3}-] (g/L)</th>
<th>[Na\textsuperscript{+}] (g/L)</th>
<th>pH</th>
<th>Conductivity at 23°C (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic</td>
<td>9.0</td>
<td>8.0</td>
<td>3.8</td>
<td>11.1</td>
<td>8</td>
<td>35.1</td>
</tr>
<tr>
<td>PWNT IEX</td>
<td>6.7</td>
<td>7.9</td>
<td>4.1</td>
<td>--</td>
<td>7.2</td>
<td>31.3</td>
</tr>
</tbody>
</table>
2.3.1.1. Study Results

The data collected in this study (Bonneau et al 2014) on the mono-selective stage indicates that more than 80% of Cl⁻ is transferred to the concentrate stream from the diluate. NOM presence in the PWNT IEX brine helped complete the separation between chlorides and sulfates. The optimum current density, with respect to separation and energy consumed, is 103 A/m². Flow rate doesn’t impact ion separation efficiency between 30 and 60 L/h. Finally, it was observed that a small amount of NOM passed through the membranes (approximately 5%).

Table 4 presents the ion selectivity of the membranes, where a selectivity of 1 means there was complete separation of the ions and 0 means no separation. Figure 12 shows the behavior of ion passage during the experiment with respect to chloride, bicarbonate, and sulfate. These graphs were used to determine the sequence of ion passage; this data suggests chloride passes across the membrane first, then bicarbonate, and almost no sulfate is transported across. The order at which ions are transported depends on the steric-hindrance effect (size of ion) and electric repulsion (charge of ion). This concept is discussed in further detail in Section 2.1 and 2.2.

Table 4: Impact of Current Density for PWNT IEX Brine Separation with Mono-Selective Stack (Bonneau et al 2014)*

<table>
<thead>
<tr>
<th>Current density (A/m²)</th>
<th>Selectivity Cl⁻/SO₄²⁻</th>
<th>Selectivity Cl⁻/HCO₃⁻</th>
<th>Selectivity HCO₃⁻/SO₄²⁻</th>
<th>Slope Cl⁻ (Mass transfer g/day)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>56</td>
<td>0.991</td>
<td>0.645</td>
<td>0.954</td>
<td>-83.8</td>
<td>0.9996</td>
</tr>
<tr>
<td>103</td>
<td>0.998</td>
<td>0.760</td>
<td>0.986</td>
<td>-159.8</td>
<td>0.9998</td>
</tr>
<tr>
<td>164</td>
<td>0.990</td>
<td>0.621</td>
<td>0.957</td>
<td>-231.1</td>
<td>0.9986</td>
</tr>
</tbody>
</table>

*Information is borrowed from Dutch reports indicating that the convention in this report is different than in the US so (,) is used instead of (,)
Non-selective membranes were also studied in this bench-scale experiment with respect to current density and brine composition. The non-selective stage used brine that was pre-treated with the mon-selective membranes. Therefore, once treated with the non-selective membranes, complete passage of chloride and bicarbonate, and up to 87% passage of sulfate was achieved. NOM in the IEX brine hindered the passage of sulfate across the membranes, and presence of monovalent ions is necessary to perform the non-selective step in this two-step ED treatment process. The optimum current density, with respect to separation and energy consumed, is 56 A/m$^2$ (Table 5).

**Table 5: Impact of Current Density for IEX Brine Separation with the Non-Selective Stack (Bonneau et al 2014)**

<table>
<thead>
<tr>
<th>Initial current density (A/m$^2$)</th>
<th>Average current density (A/m$^2$)</th>
<th>Transfer duration for 1 mS/cm (min.cm/mS)</th>
<th>Number of recirculation loops for 1 mS/cm</th>
<th>Average power (W)</th>
<th>Energy consumption for 1 mS/cm (J.cm/mS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>41.4</td>
<td>12.00</td>
<td>8.0</td>
<td>1.04</td>
<td>746</td>
</tr>
<tr>
<td>56</td>
<td>56.6</td>
<td>8.85</td>
<td>5.9</td>
<td>1.75</td>
<td>923</td>
</tr>
<tr>
<td>103</td>
<td>56.7</td>
<td>10.92</td>
<td>7.3</td>
<td>5.18</td>
<td>3385</td>
</tr>
</tbody>
</table>

*Information is borrowed from Dutch reports indicating that the convention in this report is different than in the US so (,) is used instead of (.)
2.3.2. Non-Selective Membrane Comparison

A bench-scale study was conducted to compare non-selective membranes on two brine qualities: raw IEX Andijk III Brine and brine that has been pretreated with mono-selective membranes. This study is important because it provides a comparative study of multiple types of non-selective membranes with respect to ion depletion, speed of transfer, NOM passage, and energy consumption. This section is a summary of the study presented in Lebon et al. 2014. Additional information is provided in Appendix D.

PCCell ED 64002 cell unit was used in conjunction with a pump unit and ED membranes. PCCell 64002 cell unit contains five cell pairs of anionic and cationic membranes (64 cm² active area), and the pump unit contains a flow path for each ED stream: electrolyte, concentrate, and diluate. At no point do the flow paths come in contact with each other. Figure 11 illustrates the schematic of PCCell ED 64002 cell and pump units with each respective flow path. The three brands of membranes compared include: Fujifilm, MEGA, and PCell.

2.3.2.1. Study Results

The goal of treating the IEX brine with non-selective membranes, in the case of PWNT, is mainly to remove sulfates from the IEX brine while retaining the NOM in the diluate. It is also likely that the brine treated with non-selective membranes will be treated with mono-selective membranes first. Figure 125 – Figure 130 in Appendix D presents data gathered in Lebon et al. 2014. The graphs show the performance of each membrane for raw IEX brine and brine pre-treated with mono-selective membranes. In the latter experiments, the pre-treatment step results in a lower initial concentration of chloride and bicarbonate ions (when compared with that of the raw brine). Observing the figures presented for the pre-treated brine, Mega membranes seem to outperform
the other two membranes with respect to sulfate separation and the speed of ion transfer. Mega membranes also require less energy than Fujifilm membranes, and are the second best at retaining NOM (PCCell performs best for both energy consumption and NOM retention). The disadvantages of the Mega membranes are the cost of the membranes and the size. These membranes swell resulting in a lower flow through the membranes. PCCell membranes seem to perform the second best in all parameters except sulfate transfer. Fujifilm membranes performed the worst of all three, especially with the pre-treated brine (most energy consumption, least amount of sulfate separation, most NOM passage, slowest speed of ion transfer).

The comparison between these three membranes identify important trade-offs. First, the Mega membranes performed the best for sulfate separation, however they are the least economical option, whereas PCCell membranes outperformed the others in many of the experiments, except sulfate separation. From this data, Bonneau’s conclusion about the relationship between NOM presence and sulfate passage is supported such that PCCell had the least amount of sulfate and NOM separation, whereas Mega had more sulfate transfer, which also promoted NOM passage.

2.3.3. Impact of Concentrate Conductivity

A pilot-scale study was conducted to compare the impact of initial conductivity of concentrate. This study is important because it provides a comparative study of two concentrate solutions (RO water with no salt and RO water with 18 g/L of salt) in an attempt to determine optimum initial conditions. The parameters studied in this experiment included ion depletion in the diluate stream, NOM passage, current utilization, and energy consumption. This section is a summary of the study presented in Lebon et al. 2014. Additional information is provided in Appendix D.
PCCell ED 1000H cell unit was used in conjunction with the pilot system discussed in Sections 2.3.1 and 2.3.2 (Figure 11). PCCell 1000H cell unit contains twenty-five cell pairs of anionic and cationic membranes (1000 cm² active area), 50 spacers, and three flow paths for each ED stream: electrolyte, concentrate, and diluate. As with the PCCell 64002 cell unit, the flow paths never come in contact with each other.

2.3.3.1. Study Results

The goal of this experiment was to determine the impact of concentrate conductivity on ion depletion in the diluate stream, NOM passage, current utilization, and energy consumption. This study shows that an increase in concentrate conductivity allows the same amount of chloride and bicarbonate to pass across the membrane. It also suggests that chloride has a higher current utilization and requires less energy than that of the ROW concentrate. Unfortunately, more NOM passage is observed in the NaCl concentrate trial. Refer to Appendix D for Figure 131 and Figure 132.
CHAPTER 3

METHODS AND MATERIALS

This chapter describes the experimental design, including specific equipment and laboratory procedures, used to conduct the research. This chapter also provides a framework for Chapter 4.

3.1 Materials

3.1.1 Pilot Study Materials

The EDR pilot includes two ED stacks which are operated as two separate treatment paths using two types of membranes: mono-selective (MS) and non-selective (NS) membranes. The pilot system can run in three modes: batch, continuous, and semi-continuous.

Figure 13 illustrates the flow paths for both stages of the EDR process, where the brown and orange flows indicate the diluate streams, the dark and light blue flows represent the concentrate streams, and the grey flows represent the electrolyte stream. The diluate and concentrate is pumped from the bottom of the tank, and fed into 50-micron rope filters at the base of each membrane stack. Similarly, electrolyte leaves the bottom of the tank and enters the MS ED stack, flows through the two ends of the stack, into the NS stack, and back into the tank. The electrolyte will never come in contact with the diluate nor the concentrate. Figure 115 and Figure 116 in Appendix A presents an image of the pilot system at PWNT and illustrates specific flows in and out of the tank, respectively.
Figure 13: ED Pilot Schematic, Mono- and Non-Selective Treatment Paths, Description

(A) electrolyte tank, (B) and (C) diluate and concentrate tanks for the mono-selective membranes, (D) and (E) diluate and concentrate tanks for the non-selective stack, (F) is the mono-selective stack, and (G) is the non-selective stack.

Figure 14 is a simple drawing of an ED stack (side-view). Both MS and NS stacks are designed the same way, except for the types of membranes used. The membrane cell pairs (anionic and cationic membranes with a spacer in between) sit in between membrane holders. These stacks contain 50 cell pairs. All membranes and spacers have a rubber or silicon coating around the perimeter to prevent any leaking. The stack also has an anode and cathode to enable the flow of electrons in electrolyte. Figure 117 (pg. 195) presents the membrane stack used for the pilot system.
3.1.1.1 Mono-Selective Batch Testing

Monovalent ions are separated from the IEX brine using mono-selective ED membranes. The tanks are manually filled with 200 L of diluate (raw IEX brine), 60 L of concentrate (NaCl solution), and 200 L of electrolyte. Each fluid is recirculated over time though the stack and back to feed tank as indicated in Figure 15 until the experiment is considered complete.
3.1.1.2 Mono-Selective Continuous Feed and Bleed Testing

Monovalent ions are separated from the IEX brine using mono-selective electrodialysis membranes; but in the continuous feed and bleed experiment (semi-continuous), there are two additional 1000-L tanks for external volume of diluate (IEX brine) and RO water used to automatically re-fill the system after the bleed cycle. The system will be set to bleed a certain volume of liquid (30 L for diluate, 60L for concentrate) when the respective conductivity limits are reached. The diluate bleed can either go to drain directly or into the non-selective stage.

Figure 16: Mono-selective treatment of IEX brine, continuous feed and bleed
3.1.1.3 Non-Selective Batch Testing

Multivalent ions are separated from the pre-treated IEX brine (effluent from mono-selective stage) using non-selective electrodialysis membranes. Figure 17 illustrates the flow paths used for the non-selective ED stack. The tanks are manually filled with 200 L of MS effluent, 60 L of sulfate solution, and 200 L of electrolyte.

![Figure 17: Non-selective treatment of IEX brine, batch testing](image)

3.1.1.4 Cleaning in Place (CIP)

The chemical cleaning in place (CIP) was conducted with no additional equipment. Hydrochloric acid and sodium hydroxide were the only chemicals used for the CIP. Two CIPs were compared: one with 0.1 N NaOH solution and one with 25% NaOH solution. After
completing each CIP, a demineralization test was conducted with a 30 mS/cm NaCl (saturated NaCl solution in 60 L RO water) solution in both diluate and concentrate tanks.

3.1.2 **Bench-Scale Spacer Unit**

PWNT worked with KWR Water Cycle Research Institute in Nieuwegein, NL (KWR) to modify a bench-scale spacer fouling simulator (SFS) to observe deposition of particles on the membrane surface and spacer. Pressure increase or flow decrease suggests spacer clogging. Three water qualities will be tested: raw brine, pre-treated brine with a 0.45 um filter, and pre-treated brine with a 1.0 um filter; and two different sizes of spacers will be tested. At the end of each trial, 1 liter samples were collected and analyzed for particle load before and after the cell unit to determine particle retention through the cell. The used membrane and spacers were autopsied using scanning electron microscopy (SEM) and energy dispersive atomic X-ray spectrometry (EDX) to quantify and identify the deposition.

3.1.2.1 **Pressure Increase and Particle Fouling Experiment**

The SFS includes a peristaltic pump (Figure 18), pressure meter (Figure 19), and a transparent cell. The SFS unit is designed with two transparent plastic blocks, two sheets of silicon to hold the membrane and spacer in place and prevent leaking, and fourteen bolts to close the system (Figure 20, Figure 21, Figure 22). Figure 23 illustrates the entire SFS set-up with each component labelled.
Figure 18: Masterflex peristaltic pump

Figure 19: Cerabar T PMC131

Figure 20: Spacer fouling simulator

Figure 21: Silicon sheets used for the SFS
Figure 22: Side view of SFS

Inlet

2 silicon sheets

Transparent plastic holder

Flow

Figure 23: Full SFS set-up with pump, pressure meter, tank, and SFS cell
(A) tank and propeller; (B) peristaltic pump; (C₁) pressure meter and (C₂) data logger for pressure; and (D) is the SFS

The six experiments that were conducted in the SFS are listed below with the associated materials needed:

1) Validation test with standard-sized particles (Duke Standards, NIST Traceable Polymer, \(1.5 \times 10^8\) particles with a diameter of \(5.021 \pm 0.041 \, \mu\text{m}\),) and standard spacer, \(450 \, \mu\text{m}\)

2) Pilot IEX brine and standard spacer, \(450 \, \mu\text{m}\)

3) Pilot IEX brine and big spacer, \(750 \, \mu\text{m}\)

4) Pilot IEX brine filtered with 1-micron filter and standard spacer, \(450 \, \mu\text{m}\)

5) Pilot IEX brine filtered with 5-micron filter and standard spacer, \(450 \, \mu\text{m}\)

6) Andijk III brine and standard spacer, \(450 \, \mu\text{m}\)

3.1.2.2 SEM and EDX Experiment

Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX) experiments were conducted at Wetsus European Centre of Excellence for Sustainable Water Technology in Leeuwarden, NL (Wetsus) to examine the used spacers and membranes associated with each of the six experiments above. The JEOL JFC-1200 Fine Coater was used to coat the 1 cm specimens with a gold layer of around \(15 \, \text{nm}\) is applied to the surface of the samples. This makes them conductive so electrons from the microscope will be able to go through. SEM electrons are generated and accelerated toward the sample which will generate back different kinds of radiation. Only secondary electrons are detected because they are generated from the top of the surface to \(5 \, \text{um}\) deep. Then, the 3D image is created. Only seven samples could be analyzed at one
time (twelve samples total, 6 membranes and 6 spacers) (Figure 24 and Figure 25). Then, the samples were analyzed in the JEOL JSM-6480LV scanning electron microscope (Figure 26).

*Figure 24: Samples prepared to be coated with gold (15 nm layer)*

*Figure 25: JEOL JFC-1200 Fine Coater*
3.1.3 UV-Spectrophotometer

The UV-Spectrophotometer used was a HACH DR-6000 Spectrophotometer. This instrument was used for the in-house laboratory measurements of sulfate ($\text{SO}_4^{2-}$) and total organic carbon (TOC, measuring NOM). Sulfate was measured using HACH Sulfate LR TNTplus™ 864 Reagent Set for Method 10227 (low range, 40 – 150 mg/L). Total organic carbon was measured using Total Organic Carbon, LR TNTplus™ 810 Reagent Set, DRB200 reactor with 13-mm wells, and TOC-X5 shaker for Method 10267 (low range, 1.5 – 30.0 mg/L C).
3.2 Experimental Design of Pilot Study and SFS

This section describes the experimental design of the pilot study and bench-scale SFS experiments. Detailed methods are presented in Appendix B.

3.2.1 Pilot Study Experimental Design

Performance parameters include mass transport of ions, ion selectivity of the membranes, current density, and diluate conductivity. The ED pilot was analyzed using three different types of diluate: SIX® IEX brine from the pilot facility, SIX® IEX brine from the Andijk III facility, and RO water. The pilot study included experiments on mono-selective (MS) and non-selective (NS) membrane stacks.

During the pilot experiments, in-house laboratory tests were conducted to determine the concentration of sulfate and NOM in diluate and concentrate influent and effluent. Samples were also sent to Het Waterlaboratorium N.V. Haarlem, NL (HWL) once every week to measure the concentration of sulfate, total organic carbon, sodium, chloride, bicarbonate, and pH in diluate and
concentrate influent and effluent. The importance of measuring these concentrations is to understand the mass transport of ions through the pilot system. A reduction in membrane performance can be identified by observing the passage of sulfate and NOM across the membranes.

In addition to determining the level of membrane fouling, this pilot study also assessed the impact of regular EDR and cleaning measures to prevent fouling. This pilot study observed various EDR methods and reversal times. A full EDR was studied by reversing the flows and current through the system at three different time series: 5 hours, 12 hours, and 24 hours. Pulse electric field, or “flash” reversals were also tested by only reversing the current every 2 hour(s). Two CIP methods were also analyzed, one with a lower concentration of NaOH and one with a higher concentration of NaOH. After each CIP, a demineralization test was conducted to as a control metric of membrane fouling.

3.2.1.1 Mono-Selective Batch Testing

Mono-selective batch testing was conducted at the start of the research to measure ion transport across the membranes under controlled conditions. SIX® IEX brine from the pilot facility was used to measure the ion transport across the membranes during a 5-hour time period. At the end of every batch run, the system was drained and flushed with RO water to prevent fouling due to the solution sitting stagnant. The following day, the tanks were filled again with the appropriate diluate and concentrate solutions and an EDR was performed by reversing the flow paths and direction of current through the ED stack.

At the beginning of each batch run, the concentrate tank was filled with 60 L of 75-85 mS/cm NaCl solution (RO water and saturated NaCl solution), the diluate tank was filled with 200 L of 45 mS/cm IEX brine from the PWNT pilot facility, and the electrolyte tank was filled with 100 L of 20 mS/cm sulfuric acid solution. The power was set at 45 V and 60 A.
3.2.1.2 Mono-Selective Continuous Feed and Bleed Testing

Mono-selective continuous feed and bleed testing (semi-continuous) was used to imitate full-scale operation by measuring the performance of the ED membranes with IEX brine. SIX® IEX brine from the pilot facility and Andijk III water treatment plant was used to measure the ion transport across the membranes during a 4-day continuous feed and bleed experiment. Various EDRs were conducted on this setting to compare the efficiency of each process. First, a 24-hour EDR was conducted, such that after every 24 hours, the flow paths and direction of current were reversed. Then, a 12-hour EDR was performed, such that the system was reversed at the start and end of each workday at PWNT. Finally, a flash reversal was tested, such that only the current was reversed every 2 hours. The pilot was not run over the weekend.

At the end of every week, the system was drained and a CIP was performed. The purpose of the CIP was a preventative measure to avoid serious damage to the membrane before the end of the research.

At the beginning of each continuous run, the concentrate tank was filled with 200 L of 75-85 mS/cm NaCl solution (RO water and saturated NaCl solution), the diluate tank was filled with 200 L of 45 mS/cm IEX brine from the PWNT Pilot Facility or 25 mS/cm IEX brine from the Andijk III water treatment facility, and the electrolyte tank was filled with 100 L of 20 mS/cm sulfamic acid solution (sulfuric acid was used when sulfamic acid was not available). The pilot was set to bleed the diluate once the conductivity reached 19 mS/cm, for the pilot brine and 14 mS/cm for the Andijk III brine. Once diluate is bled from the system, fresh brine is pumped into the diluate tanks from a 1000-L external storage tank to continuously run the ED stack. The pilot was also set to bleed the concentrate at 90 mS/cm for both trials (pilot and Andijk III brine). The power was set at 45 V and 60 A for the entire duration of the experiment.
3.2.1.3 Non-Selective Batch Testing

The purpose of the batch tests with non-selective membranes was to observe the separation of sulfate ions from NOM in the IEX brine. SIX® IEX brine desalinated using the mono-selective membranes is pumped into the non-selective stage. This experiment was run in batch for five hours. At the end of every batch run, the system was drained and flushed with RO water to avoid stagnant solution.

At the beginning of each batch run, the concentrate tank was filled with 60 L of 10 mS/cm \( \text{Na}_2\text{SO}_4 \) solution (RO water and sodium sulfate salt), the diluate tank was filled with 200 L of 19 mS/cm IEX Pilot Brine or 14 mS/cm IEX Andijk III Brine from the mono-selective stage, and the electrolyte tank was filled with 200 L of 20 mS/cm sulfuric or sulfamic acid solution. The power was set at 45 V and 60 A.

3.2.1.4 Cleaning in place (CIP)

The purpose of conducting CIPs periodically during the research was a preventative measure to minimize serious fouling of the membranes. Only one CIP was conducted while running the system in batch, and a CIP was conducted once every week while running the system continuously in the feed and bleed setting.

A demineralization test was conducted after every CIP to analyze how well ions pass through the membranes with respect to the percent decrease of diluate conductivity overtime. This test is a controlled measurement using RO water and pure sodium chloride solution. If ion passage decreases over time, it indicates that membrane performance also decreases. Concentrate and diluate tanks were filled with 100 L 30 mS/cm NaCl solution. The electrolyte solution contained \( \text{H}_2\text{SO}_4 \) with a conductivity of approximately 20 mS/cm. Voltage was set at maximum power.
(approximately 61 V) and the current was fixed at 6 A. Temperature and pH measurements were taken every 5 minutes during the 30-min test.

3.2.2 **Bench-Scale Spacer Unit**

The first step of the spacer fouling unit was to validate the experiment by using a known solution of particles and observing particle retention. The spacer fouling cell design options are presented in Appendix G. The chosen cell design was “Option 2” which includes two silicon sheets to seal the cell and an electronic pressure gauge because it was the most feasible option with respect to the scope, schedule, and budget for the spacer clogging experiment.

At the end of each experiment, influent and effluent samples were taken from the spacer unit for particle count analysis to determine whether or not particles were being removed across the length of the cell. The samples collected were sent to KWR to be analyzed with a particle counter. Additionally, samples of the spacer and membrane were also sent HWL to measure the amount of ATP present at the inlet and outlet of the cell unit. The remaining spacers and membranes were set aside to dry. These samples were then analyzed with SEM and EDX at Wetsus to determine the constituents that adhered to the surface of the spacers and membranes.

After conducting the bench-scale experiments and analyzing the ATP data from HWL, samples of IEX brine from Andijk III and denitrified IEX brine were gathered for biological production potential (BPP) and assimilable organic carbon (AOC) analyses at HWL. The purpose of the AOC and BPP experiments were to determine if there was a potential for biofouling in the ED stack.
3.2.3 Laboratory Experiments

3.2.3.1 In-House Experiments

Sulfate, total organic carbon, pH, and temperature were measured in the PWNT research lab. All glassware was cleaned with milli Q water before and after all experiments. Sulfate and NOM were measured using the HACH DR-6000 in conjunction with HACH test kits. The procedures associated with measuring sulfate and NOM are included in Appendix C.

3.2.3.2 Het Waterlaboratorium N.V. Haarlem

HWL is a contract laboratory located in Haarlem, Netherlands and is independent from PWNT. HWL is accredited by the Dutch Accreditation Council RvA and follows standard regulations set by ISO/IEC 17025:2005.

During pilot testing, samples were sent to HWL once every week to measure the initial and final concentrations of sodium, chloride, bicarbonate, sulfate, total organic carbon, conductivity, and pH. During the SFS bench-scale experiments, ATP samples were prepared at PWNT and sent to HWL to measure the amount of ATP on the spacer and membrane. Additionally, samples of IEX Pilot Brine, IEX Andijk III Brine, and IEX Denitrification Brine were sent to HWL for LC-OCD measurements, as well as measurements of BPP and AOC.

3.2.3.3 SEM/EDX Analysis

The following spacer/membranes pairs were gathered to be analyzed by SEM/EDX and put into a desiccator to completely dry:

a. 450 um Spacer, Standard Test, Inlet
b. AEM Membrane, Standard Test, Inlet
c. 450 um Spacer, Standard Test, Outlet
d. AEM Membrane, Standard Test, Outlet

e. 450 um Spacer, 10-Micron Filtered Brine, Inlet

f. AEM Membrane, 10-Micron Filtered Brine, Inlet

g. 450 um Spacer, DNF Brine, Inlet

h. AEM Membrane, DNF Brine, Inlet

i. 750 um Spacer, Large Spacer Test, Inlet

j. AEM Membrane, Large Spacer Test, Inlet

k. 450 um Spacer, Andijk III Brine, Inlet

l. AEM Membrane, Andijk III Brine, Inlet

The samples were then taken to Wetsus to be analyzed with SEM/EDX laboratory equipment and analyzed with the help of Wetsus staff.
CHAPTER 4

RESULTS AND DISCUSSION

This chapter presents the experimental data and explanation of these results. This chapter discusses the concepts of how conclusions and recommendations were made.

4.1. Mono-Selective Membrane Pilot Test Results

Two experiments were conducted to observe the impact of batch operation versus continuous feed & bleed operation, various brine qualities (IEX Pilot Brine and IEX Andijk III), and EDR frequencies.

4.1.1 Batch Pilot Operation

Batch experiments were conducted to observe the differences of 5-hr EDR versus 30-hr EDR frequencies. Figure 28 illustrates the conductivity data collected during the 5-hr EDR batch test (five batch runs were conducted dis-continuously, totaling 25 hours) with IEX Pilot Brine and a full EDR every 5 hours. After each 5-hour batch run, the membranes were rinsed with RO water, then, the diluate and concentrate flows and electrodes were reversed. Time, initial conductivity of diluate and concentrate, and voltage were controlled, whereas current and change in conductivity were variable.

On average the diluate conductivity decreased 30.2 ± 1.8 mS/cm, and the concentrate conductivity increased 37.1 ± 4.1 mS/cm. During this 5-hr EDR batch test, there was no change in membrane performance with respect to change in diluate and concentrate conductivity. This could
be due to two factors: rinsing the membranes with RO water and/or frequently conducting EDRs. Typically, electrodialysis operation does not include a long rinsing period with RO water as done here, but rather a quick flush of the system to remove excess concentrate and diluate in the stack. However, the RO rinse was necessary because the system needed to be shut down every evening. Therefore, if the membranes were not rinsed, there is a higher change of organic fouling due to the IEX brine sitting stagnant in the stack. The EDR could also be preserving membrane performance by removing any NOM molecules that may have adhered to the surface of the membranes. While the purpose of an EDR is to preserve membrane performance, it is more likely the preservation was due to the RO rinse rather than the EDR.

It is also important to note the higher variation on the reversed side of the membrane. In Figure 28, the conductivity of the concentrate is very scattered, especially once it exceeds 100 mS/cm. This variation is likely due to one of the conductivity meters not being calibrated or the conductivity was out of range. The conductivity meters have an operating range up to 20 mS/cm, which is even lower than the diluate conductivity.
Figure 28: Batch, 5 hr-Reversal, Diluate and Concentrate Conductivity

Figure 29 presents the behavior of diluate conductivity and current density during the 25-hr batch test with IEX Pilot Brine and a full EDR every 5 hours. The average current density of each 5-hr test was 17.5 ± 1.0 mA/cm², and there was no decrease in membrane performance with respect to current density. However, a lower current density can be seen during the EDR. By separating the current densities into two categories, normal operation and EDR, there is a decrease in the variation of the data. During normal operation, the average current density is 18.1 ± 0.7 mA/cm², whereas the average current density of the EDR is 16.6 ± 0.5 mA/cm². This difference could mean that one side of the membrane is fouled more.
Figure 29: Batch, 5-hr Reversal, Diluate Conductivity and Current Density

Figure 30 illustrates the conductivity data collected during the 30-hr EDR batch test (eleven 5-hr batch runs were conducted dis-continuously, totaling 55 hours) with IEX Pilot Brine and a full EDR after 30 hours. Similar to the previous study, the membranes were rinsed after each 5-hr batch run. After six 5-hour trials of batch runs in normal ED operation, the membranes were rinsed with RO water, then the diluate and concentrate flows and electrodes were reversed. Time, initial conductivity of diluate and concentrate, and voltage were controlled, whereas the current and change in conductivity were variable.

On average, the diluate conductivity decreased 30.1 ± 1.0 mS/cm, and the concentrate conductivity increased 40.6 ± 9.1 mS/cm. During this 30-hr EDR batch test, there was no change in performance with respect to the ability of the membranes to transfer ions. Similar behavior of the concentrate conductivity on the reversed side of the membrane is also prevalent in this experiment, which further supports the hypothesis that the conductivity meter was not calibrated...
or out of range. When an EDR is conducted for the batch experiments, the tank that was originally filled with diluate, is now filled with concentrate, and vice versa. Therefore, in this 30-hr EDR experiment, the concentrate conductivity has high variability only when concentrate is in the diluate tank. This suggests that the conductivity meter in the diluate flow path is not properly calibrated. The full-scale design will need to carefully examine the acceptable conductivity range and calibrate the meters as directed in the operations manual.

![30-hr EDR](image)

*Figure 30: Batch, 30-hr Reversal, Diluate and Concentrate Conductivity*

Figure 31 presents the behavior of the diluate conductivity and current density during the 30-hr EDR batch test with IEX Pilot Brine. Similar to the 5-hr EDR frequency, the average current density of each 5-hr trial was $18.5 \pm 0.9$ mA/cm$^2$, and there was no decrease in membrane performance with respect to current density. There was also very little difference in the current densities with respect to the side of the membranes in use (i.e. regular or reverse). By separating the current densities into two categories, the average regular current density is $18.1 \pm 0.7$ mA/cm$^2$, 
whereas the average EDR current density is 19.0 ± 1.1 mA/cm². This refutes the hypothesis that membrane performance changes depending on the side of the membrane.

![Figure 31: Batch, 30-hr Reversal, Diluate Conductivity and Current Density](image)

4.1.1.1. Ion Passage Across Membranes in Batch Experiments

Ion passage per membrane area and per current density is an indication of stack performance. Stack performance is high when ion passage per membrane area or current density is high. Ion passage would decrease if the applied voltage to the stack is lowered because there is less transfer of electrons in the electrolyte at the anode and cathode. Additionally, as ion concentration decreases in solution, the current density will also decrease because the solution is less conductive. This parameter can be further assessed as the “speed of transfer”, which is the rate ions move across the membrane per area and time. Therefore, as less ions are present in solution,
the speed of transfer also decreases due to the normal decrease of current density. Speed of transfer is calculated as the flow of ions per area membrane and time (Eq. 21), where $\Delta meq_i$ is the change of total equivalent mass of an ion, membrane area is the total surface area of cation and anion exchange membranes in the ED stack (560 cm$^2$), and $\Delta t$ is the duration of the experiment:

$$\text{Speed of Transfer} = \frac{\Delta meq_i}{\text{Membrane Area} \times \Delta t}$$  \hspace{1cm} (22)

The faster the ion transfer means permselectivity is high, electrical resistance is low, and the membranes have good IEC as discussed in the Literature Review Chapter (Sata 2007, Strathmann 2010, Bernardes et al 2014).

Good membrane performance suggests there is a high speed of transfer and low membrane resistance, whereas decreasing membrane performance shows a low speed of transfer because of increased membrane resistance preventing ions to pass through the membrane. Figure 32 presents the speed of ion transfer during the 5-hr EDR and 30-hr EDR batch experiments. Ion passage data is similar to the speed of transfer; it is presented in Appendix E. The data suggests there is no decrease in performance due to a relatively stable speed of transfer, such that there is a high speed of monovalent ion transfer and a low speed of multivalent ion transfer. Figure 33 shows the average speed of transfer for each ion with variation of 1-standard deviation away from the mean. This data also suggests that the speed of transfer for chloride and bicarbonate significantly exceed that of the sulfate ions, indicating desirable membrane performance.
The final measure of membrane performance over time was the percentage of ion passage from the diluate into the concentrate. Percent ion passage into the concentrate is an indicator of membrane performance, whereas it is desirable to have high passage of monovalent ions (chloride,
bicarbonate, and sodium), and low passage of multivalent ions (NOM and sulfate). Ion selectivity oftentimes decreases as membranes age (Ghalloussi et al 2013), which indicates a greater amount of multivalent ions passing across the membrane as discussed in Section 2.2.2. Figure 34 plots the percent passage out of the diluate stream, and the percent passage of ions into the concentrate stream. Ion concentration was adjusted to account for water passage from the diluate into the concentrate (approximately 20 L per trial).

Percent ion decrease in diluate was calculated using Equation 2523, and percent increase in concentrate concentration was calculated in Equation 26:

\[
\left(1 - \frac{\text{final diluate conductivity}}{\text{initial diluate conductivity}}\right) \times 100\% = \% \text{ Decrease in Diluate} \quad \text{Equation 24}
\]

\[
\left[\frac{(\text{final concentrate mg/L} - \text{initial concentrate mg/L}) \times 60 \text{ L}}{(\text{initial diluate mg/L}) \times 200 \text{ L}}\right] \times 100\% = \% \text{ Increase in Concentrate} \quad \text{Equation 25}
\]

![](image.png)

*Figure 34: Percentage of Ion Passage into Concentrate, Batch Experiments*
Over an accumulated 70 hours of operation, stable performances of the membranes were recorded on all parameters. First, good selectivity with passage of monovalent ions was observed; ion passage of chloride, bicarbonate and sodium was respectively recorded at 83 to 94%, 58 to 71% and 60 to 64%, while sulfate and NOM are retained at 96 and 99%. The relatively low passage of sodium is explained by the electroneutrality that needs to remain in the diluate when sulfate ions are present. Second, there was no sign of increase in membrane resistance at neither of the EDR frequencies. This observation cannot be directly linked to the stability of the process nor to the reversal frequency since rinsing was performed every night to avoid stagnation. In order to eliminate RO rinsing of the membrane and produce conclusive data of the impact of the frequency of reversals, the process was altered to run continuously, which is the topic of the next section.

4.1.2 Continuous Feed and Bleed (F&B) Pilot Operation

596 hours of continuous feed & bleed (F&B) experiments were recorded to observe the impact of various brine qualities (IEX Pilot Brine and IEX Andijk III) and of EDR frequencies.

Under F&B conditions, the concentrate conductivity increases until 90 mS/cm, and the diluate conductivity decreases to 19 mS/cm or 14 mS/cm depending on brine quality. Once the upper conductivity limit in the concentrate and the lower conductivity limit in the diluate are reached, the pilot discharges concentrate or diluate, and feeds RO water or raw IEX brine into the respective tanks (Figure 13). From the time diluate or RO water feeds into the tank to when it bleeds is considered one “cycle.” Objectives for the F&B pilot operation are two-fold:

- Follow operational parameters (conductivity and current density) overtime to observe any membrane fouling or ageing; and
- Assess the impact of reversal frequency.

Results are obtained on 2 types of brine:
4.1.2.1 Operational Data with IEX Pilot Brine

The pilot was run on continuous F&B for 210 hours with IEX Pilot Brine and two EDR frequencies: 24-hr EDR and 12-hr EDR.

4.1.2.1.1 Operational Data, 35-hour Snapshot of F&B

Figure 35 and Figure 36 display a 35-hour snapshot of data recorded on the pilot, which illustrate system behavior during F&B operation. Figure 35 shows concentrate and diluate conductivities with a 12-hr reversal directly after a CIP. As ions are being transported from the diluate stream into the concentrate stream, diluate conductivity decreases to 19 mS/cm and concentrate conductivity increases to 90 mS/cm. The initial conductivity in the tank of each diluate cycle ranges from 21-23 mS/cm, which is half than that of the raw brine (approximately 45 mS/cm) because the bleeding mechanism drains about 30 L of diluate before re-filling the tanks. Therefore, 30 L raw diluate (45 mS/cm) is being diluted in 170 L of treated diluate (19 mS/cm). This same concept is true for the concentrate; the initial conductivity of the concentrate is 20 mS/cm and increases to 90 mS/cm. Once the systems bleeds 90 mS/cm concentrate, it feeds pure RO water which decreases the conductivity to 75 mS/cm.

Figure 36 shows current density associated with diluate conductivity. The snapshot clearly defines the behavior of current density and diluate conductivity. The depletion of conductive ions on the diluate side causes the stack resistance to increase and current density to decrease as ions are being transported from the diluate into the concentrate. This behavior is normal and not an
indication of fouling because current density is restored when new ions are brought to the diluate at the beginning of each cycle.

![Diluate Conductivity and Concentrate Conductivity](image)

*Figure 35: F&B 35-hr Snapshot, IEX Pilot Brine, Diluate and Concentrate Conductivity*

![Diluate Conductivity (mS/cm) and Current Density (mA/cm²)](image)

*Figure 36: F&B 35-hr Snapshot, IEX Pilot Brine, Diluate Conductivity and Current Density*

4.1.2.1.2. **Overview of Operation Data, 210 Hours of Operation**

Figure 37 shows the overview of diluate and concentrate conductivity during 210 hours of F&B pilot operation and therefore displays a number of previously described “cycles”. After each...
RO rinse or CIP, the tanks are filled with raw brine and 20 mS/cm solution of RO water and dissolved NaCl. During the 210 hours displayed, notable events include:

- The change in reversal frequency which impacts are developed later in this chapter.
- Instability in the first 50 hours due to an intentional drop in electrolyte conductivity.
- A change in electrolyte type: from sulfamic acid to sulfuric acid marked by the green dotted line at 115h which impact is also discussed later in this chapter.
- Two CIPs at 81 and 210 hours and three RO rinse at 27, 57 and 115 hours.

Figure 38 shows diluate conductivity and current density during 210 hours of F&B pilot operation. As observed in the snapshot, current density is a function of the electrical gradient across the membranes. Therefore, as diluate conductivity decreases and concentrate conductivity increases, the current density will decrease. Current density can also be a measure of membrane performance over time because it is negatively affected by the increase of electrical resistance either from the membrane or from the stack. Membrane electrical resistance increase is typically associated to foulant deposition, while a depletion of ions (low conductivities) in either concentrate or diluate would cause an increase in stack resistance. If current density doesn’t restore after diluate and concentrate conductivities are back to original conditions, this suggests membrane resistance also increases. That phenomenon for example is obvious between 25 and 55 hours, when the current density continuously decreases, under the effect of deposition of material onto the surface of the membrane. If a reversal cannot restore the conductivity, it is considered fouling. For example, after 150 hours would be considered fouling, the frequent reversals are not efficient to restore current density, which ends up slowing the transfer of ions.
Figure 37: F&B for 210 hrs of Operation, Pilot Brine Diluate and Concentrate Conductivity
Figure 38: Feed and Bleed for 210 hrs of Operation, Pilot Brine Diluate Conductivity and Current Density
Figure 39 shows a comparison of operational data when using two types of electrolyte: sulfamic acid (H₃NSO₃) and sulfuric acid (H₂SO₄). The data raises a hypothesis that sulfuric acid is not an effective electrolyte solution because ion transfer is hindered in the bottom-most graph. The reason for this could be that the fixed ions on the membranes are quaternary amines and sulfonic acid. Therefore, with an electrolyte medium which includes a nitrogen component may increase membrane performance. During the two runs with sulfamic acid (C-H3NSO3, 1 and 2), the rate at which the concentrate reached 90 mS/cm was higher than that of the run with sulfuric acid (C-H2SO4); during 74 hours of operation with sulfamic acid yielded 7 concentrate cycles, whereas 94 hours of operation with sulfuric acid yielded 3.5 concentrate cycles. In the graph below, operational data with a low electrolyte conductivity (<20 mS/cm) was omitted. This hypothesis should be researched further to determine the effects of type of electrolyte because it was not researched in this thesis.

![Electrolyte Comparison, H2SO4 vs H3NSO3](image)

*Figure 39: Electrolyte Comparison*
4.1.2.2 Operational Data with Full-Scale, IEX Andijk III Brine

The pilot was run on continuous feed & bleed for 386 hours with IEX Andijk III Brine. During this experiment, the pilot was tested with two EDR frequencies: 12-hr EDR, 24-EDR with flash reversal, and 50-hr EDR with flash reversals.

4.1.2.2.1. Operational Parameter Definition

After switching the brine quality from IEX Pilot Brine to IEX Andijk III Brine, there is a necessity to redefine the lower conductivity limit on the diluate side to recover the higher possible amount of chloride without significantly increasing the system resistance. Figure 40 shows the data collected during exploration for lower diluate conductivity limits:

- First, 14 mS/cm limit was selected, with rather stable operation;
- Then, the limit is reduced to 10 mS/cm, an important decrease in current density and a visible slow-down of ion passage are observed due to lower concentrations at 10 mS/cm;
- Finally, when set to 12 mS/cm, the data seems well at first but then a significant decrease in current density occurs after 42 hours.

Therefore, the diluate conductivity limit was set at 14 mS/cm to preserve membrane performance and achieve a more consistent current density.

In addition to achieving a suitable current density, the behavior of concentrate conductivity was also considered because a 90 mS/cm concentrate solution is the target product. Figure 41 shows the diluate and concentrate conductivity during the snapshot as in Figure 40. The concentrate conductivity rapidly increases between 0-15 hours when the diluate conductivity limit was at 14 mS/cm. When the diluate conductivity limit was set to 12 mS/cm, the concentrate conductivity never reached 90 mS/cm. In fact, the concentrate conductivity decreased from 88
mS/cm to 86 mS/cm between 45 and 62 hours of operation. This data further supports the decision to operate the F&B process with a diluate conductivity limit at 14 mS/cm.

Figure 40: F&B 47-hr Snapshot, Diluate Conductivity Limit, Current Density Consideration

Figure 41: F&B 47-hr Snapshot, Diluate Conductivity Limit, Concentrate Consideration
4.1.2.2.2. **Operational Data, 90-Hour Snapshot of F&B**

Figure 42 and Figure 43 show the conductivity and current density data collected during F&B operation with IEX Andijk III Brine and a 12-hr EDR. This data suggests that one side of the membrane is performing better than the other. The current density and the slope of concentrate conductivity increase after the EDR at 84, 106, and 130 hours, which suggests there is a higher rate of ion transfer across the membranes. The current density and slope of concentrate conductivity decrease after the EDR at 90, 115, and 140 hours. The reversed side of the membrane was frequently used during the overnight runs, typically 16 hours, versus the daytime runs, typically 8 hours. Therefore, decreased membrane performance could be attributed to longer EDRs.

![Diluate Conductivity and Concentrate Conductivity](image)

*Figure 42: F&B 90-hr Snapshot, Diluate and Concentrate Conductivity, 12-hr EDR*
Figure 43: F&B 90-hr Snapshot, Diluate Conductivity and Current Density, 12-hr EDR

4.1.2.2.3. **Operational Data, Flash Reversal Experiment**

Flash reversals are different from full EDRs because only the electrodes are reversed, as opposed to reversing the electrodes and flow paths. The pilot study looked at two flash reversal times: 3-min and 5-min every 2 hours. Figure 44 and Figure 45 show conductivity and current density data for a 23-hr snapshot with a 5-min flash reversal. The flash reversals are illustrated as the dotted line on the graphs. During a flash reversal, ion passage is transported with the electrical gradient rather than against it. Therefore, the 5-min reversal shows diluate conductivity increasing and concentrate conductivity decreasing.
Figure 44: Feed and Bleed 23-hr Snapshot, IEX Andijk III Brine, Diluate and Concentrate Conductivity, 5-min Flash Reversal

Figure 45: Feed and Bleed 23-hr Snapshot, IEX Andijk III Brine, Diluate Conductivity and Current Density, 5-min Flash Reversal
Figure 46 and Figure 47 display a 3-min flash reversal to determine if salt passage in the undesirable direction could be limited with the same benefits of reducing deposition on the membrane surface. In theory, this method would be more effective since the diluate conductivity is not increasing as much as with the 5-min flash reversal. However, an adverse behavior was observed: membrane performance significantly decreased such that it took 47 hours for the concentrate to increase 30 mS/cm. The decreased system performance in the 3-min flash reversal may not be long enough to remove the deposited foulants on the surface of the membranes. Therefore, foulants continue to build up, while the flash reversals transport ions in the opposite direction for 3-min.

![Graph of Dilute and Concentrate Conductivity](image)

**Figure 46: Feed and Bleed 54-hr Snapshot, IEX Andijk III Brine, Diluate and Concentrate Conductivity, 3-min Flash Reversal**
4.1.2.2.4. **Overview of Operational Data, 386 Hours of Operation**

*Figure 48* and *Figure 49* show the overview of conductivity and current density during 386 hours of F&B operation, which illustrate the previously described EDRs and flash reversals. Similar to the pilot operation with IEX Pilot Brine, these figures display diluate and concentrate cycles. After each RO rinse or CIP, the tanks are filled with raw brine and 20 mS/cm solution of RO water and NaCl. During the 386 hours of operation, notable events include:

- A change in reversal type: EDR marked with a dotted line, and flash reversal marked with bursts of high current densities,
  - EDRs every 12-hrs during the first 150 hours;
  - 5-min flash reversal every 2 hours from 153-228 and 320-386 hours; and
  - 3-min flash reversal every 2 hours from 228-320 hours
- Instability in membrane performance in the first 50 hours due to experiment on operational parameters,

- Current density varied depending on operational conditions, but stayed relatively constant during entire experiment, and

- Three CIPs at 153, 228, 321, and 386 hours, and an RO rinse at 62 hours. Impact of the two methods of cleaning is developed later in this chapter.
Figure 48: Feed and Bleed for 386 hrs of Operation, IEX Andijk III Brine Diluate and Concentrate Conductivity
Figure 49: Feed and Bleed for 386 hrs of Operation, IEX Andijk III Brine, Diluate Conductivity and Current Density
4.1.3 Preventative Cleaning Strategies

A CIP was performed before the first batch experiment and after each week of running the ED system on the F&B setting. CIPs acted as a preventative cleaning strategy for the membranes, which will in theory remove all reversible fouling. A demineralization test was conducted after each CIP to determine the effectiveness of the cleaning method and if membrane performance has decreased over time. Demineralization tests were labelled “M#, T#”, where “M” is the cleaning method and “T” is the trial. M1 used a 0.1 N HCl and 0.1 N NaOH solutions, and M2 used 0.1 N HCl and 2.5% NaOH solutions. One demineralization test (M1, T8R) was conducted as an EDR to analyze the reverse side of the membrane.

Figure 50 shows the demineralization rate after each CIP, which was calculated using Eq. 20 in Section 2.2.4. Over the course of the research, the demineralization rate did not significantly decrease. In fact, the first three demineralization tests show increasing demineralization rate (M1, T1; M2, T1; and M1, T2), which suggests that the preventative CIP improved membrane performance and held it consistent thereafter. A reason why the first three demineralization rates were slightly lower could be due to some resistant fouling. Improved membrane performance is further supported in the membrane evaluation discussed in Section 4.1.5. However, after consistently cleaning the membranes, the stubborn foulants are removed. Another important trial to note is M1, T8R, which was conducted to compare the performance of the membranes in the reverse direction to that in normal operation; M1, T8 and M1, T8R were conducted after the same CIP. This can be compared to the data found in Figure 42 and Figure 43, where a difference in current density can be seen on the reversal side of the membranes. It is also important to note that
the demineralization test was a 30-minute experiment. Therefore, the total demineralization is only 15% for most experiments.

**Figure 50: Demineralization Rate After CIP**

Figure 51 shows the total percent demineralization at the end of the experiment. This graph further supports the data in Figure 50, such that there is an increasing demineralization in the first three experiments, demineralization is held relatively constant from T3-T8, and the reversed side of the membrane has slightly decreased performance.
A second measure of membrane performance with respect to the demineralization test, is voltage during the 30-min experiment. Unlike the batch and feed & bleed experiments, the demineralization test holds the current constant, while voltage is variable. Therefore, when voltage is high, the system is using a high amount of energy to transport ions, whereas a lower voltage means the system requires less energy to transport ions.

Figure 52 shows voltage during each 30-min experiment. M1, T1-T2 have the highest voltage, and M1, T3, T7 and T8 have the lowest voltage for the experiment. M1, T1-T2 also had low demineralization rates compared the rest of the trials, which confirms the conclusion that membrane performance increased over the first three trials. While the voltage is a varying parameter, it stays relatively constant throughout the duration of the experiment.
4.1.4 NOM and Sulfate Passage

Recovery of sodium chloride in the concentrate is being considered as a potential regeneration solution for the SIX® ion-exchange resins. Therefore, it is important to quantify natural organic matter (NOM) and sulfate concentrations in the concentrate stream to determine the quality of the recovered solution. If NOM or sulfate concentrations are too high in the recovered solution, it cannot be used for regeneration because resins have a high affinity towards NOM and sulfate. Sodium chloride concentration must be in excess when compared to that of NOM or sulfate. Key objectives in considering NOM and sulfate contamination in the concentrate include:

- Determine concentration of NOM and sulfate in the final concentrate product at 90 mS/cm,
- Compare concentration of sodium chloride to that of NOM and sulfate, and
Compare concentration of NOM and sulfate in concentrate produced with IEX Pilot and IX Andijk III Brines.

4.1.4.1. NOM and Sulfate Passage, F&B Pilot Brine Operation

Once the conductivity of the concentrate reaches 90 mS/cm (30 g/L Cl\(^-\)) during the F&B operation, the system discharges concentrate (on full-scale this would not be discharged, but rather stored for re-use in SIX®). Figure 53 displays the average NOM (measured in total organic carbon (TOC)) and sulfate concentrations during F&B operation with IEX Pilot Brine. The average NOM concentration in the concentrate is approximately 93 mg/L ± 15 mg/L, whereas the sulfate is on average 416 mg/L ± 156 mg/L. Figure 54 illustrates the diluate and concentrate concentrations of sulfate and NOM during pilot operation. Concentrations in IEX Pilot Brine were measured by taking samples of the diluate in the tank at the beginning of a cycle. Sulfate and NOM concentration in the diluate increase after 115 hours. Diluate with high sulfate and NOM is carried over into the concentrate during the manual EDRs (pilot does not have the ability to flush system before an EDR), which increase the concentrations of sulfate and NOM in solution (Figure 55). Therefore, ion selectivity conclusions cannot be made from this data.
Figure 53: Sulfate and NOM (mg/L) in Concentrate at 90 mS/cm, Pilot Brine Operation

Figure 54: Sulfate and NOM in Concentrate and Diluate, Pilot Brine Operation
Figure 55 displays NOM and sulfate concentrations in the concentrate before and after an EDR. This parameter was measured because the pilot does not have a flushing mechanism, which results in diluate being carried over into the concentrate stream and concentrate is carried over into the diluate stream after each EDR. After one EDR, the sulfate concentration increases 83 mg/L and NOM concentration increases 11 mg/L. This concept contributes to the behavior observed in Figure 54 of sulfate and NOM concentrations in the concentrate.

![Impact of Reversal on Ion Concentration, Pilot Brine](image)

*Figure 55: Impact of EDR on Ion Concentration in Concentrate, Pilot Brine Operation*

While it is important to determine final concentrations of NOM and sulfate in the concentrate, it is also valuable to understand the variation of sulfate and NOM concentrations in the diluate. Figure 56 and Figure 57 show the average concentration in the diluate tank at the beginning and at the end of cycles when the pilot is discharging. On average, sulfate concentration is $6.8 \pm 1.1$ g/L at the beginning of diluate cycles and $6.7 \pm 1.2$ g/L at the end of cycles. On average,
NOM concentration is $510 \pm 75$ mg/L at the beginning of diluate cycles and $502 \pm 91$ mg/L at the end of cycles.

**Figure 56: Sulfate Concentration in Diluate, Pilot Brine Operation**

**Figure 57: NOM Concentration in Diluate, Pilot Brine Operation**
Table 6 presents ion concentration data obtained from HWL on the raw diluate feed and final concentrate at 90 mS/cm, which shows the influent and effluent of the pilot system. From this table, chloride to NOM and chloride to sulfate concentrations can be calculated to determine the ratio of chloride to the unwanted constituents. The ratio of chloride to unwanted constituents is important because the resins have a high affinity towards NOM and sulfate due to their charge. Therefore, chloride concentration needs to be at least one order of magnitude greater than the contaminants (sulfate and NOM) to maintain the resin’s ion exchange recovery capacity. In pilot operation with IEX Pilot Brine, chloride is in excess when compared to NOM and sulfate:

- Chloride to NOM: $1900 \frac{g}{L} \text{Cl}^{-} : 1 \frac{g}{L} \text{TOC}$

- Chloride to sulfate: $60 \frac{g}{L} \text{Cl}^{-} : 1 \frac{g}{L} \text{SO}_{4}^{2-}$

Table 6: Ion Concentration in Raw Diluate and Final Concentrate

<table>
<thead>
<tr>
<th></th>
<th>Chloride g/L</th>
<th>Bicarbonate g/L</th>
<th>Sodium g/L</th>
<th>NOM mg/L</th>
<th>Sulfate g/L</th>
<th>Conductivity mS/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Diluate Feed</td>
<td>11</td>
<td>7</td>
<td>15</td>
<td>510</td>
<td>7</td>
<td>45</td>
</tr>
<tr>
<td>Concentrate Final</td>
<td>36</td>
<td>14</td>
<td>29</td>
<td>19</td>
<td>0.6</td>
<td>84</td>
</tr>
</tbody>
</table>

4.1.4.2. NOM and Sulfate Passage, F&B Andijk III Operation

Figure 58 displays NOM (measured as TOC) and sulfate concentrations during F&B operation with IEX Andijk III Brine. Average NOM concentration is approximately 61 mg/L ± 17 mg/L, whereas sulfate is 381 mg/L ± 108 mg/L. Sulfate and NOM concentrations in the diluate can also be observed in Figure 59. Concentrations of IEX Andijk III Brine were measured by taking samples of the raw diluate feeding into the tank at the beginning of a cycle. Similar to the
IEX Pilot Brine F&B study, sulfate and NOM were carried over into the concentrate during manual EDRs, therefore adding some error to these measurements Figure 60.

**Figure 58:** Sulfate and NOM (mg/L) in Concentrate at 90 mS/cm, Andijk III Brine Operation

**Figure 59:** Sulfate and NOM in Concentrate and Diluate, Andijk III Brine Operation
Figure 60 displays NOM and sulfate concentration before and after one EDR. NOM and sulfate concentrations in the concentrate increase due to the high concentrations of the constituents in the diluate. After one EDR, the sulfate concentration increases 34 mg/L and NOM concentration increases 36 mg/L. Compared to the carry-over of diluate when using the IEX Pilot Brine (Figure 55), the IEX Andijk III Brine shows more NOM contamination, but significantly less sulfate contamination.

![Impact of Reversal on Ion Concentration, Andijk III Brine](image)

**Figure 60:** Impact of EDR on Ion Concentration in Concentrate, Andijk III Operation

Figure 61 and Figure 62 show the average concentration of raw diluate feeding into the tank at the beginning and the effluent at the end of cycles when the pilot is discharging. On average, sulfate concentration is $4.7 \pm 0.85$ g/L at the beginning of diluate cycles and $4.6 \pm 0.65$ g/L at the end of cycles. On average, NOM concentration is $349 \pm 50$ mg/L at the beginning of diluate cycles and $337 \pm 42$ mg/L at the end of cycles. Sulfate and NOM concentrations in the Andijk III diluate are different than that of the brine produced at the pilot facility (details in Table 1). Even with
varying conditions, the change in sulfate and NOM concentration are comparable to the change in concentration in the pilot brine.

Figure 61: Sulfate Concentrate in Diluate, Andijk III Brine Operation

Figure 62: NOM Concentration in Diluate, Andijk III Brine Operation
Table 7 presents ion concentration data obtained from HWL on the raw diluate feed and final concentrate at 90 mS/cm, which shows the influent and effluent of the pilot system. From this table, chloride to NOM and chloride to sulfate concentrations can be calculated to determine the ratio of chloride to the unwanted constituents. Here, the chloride to NOM and sulfate ratios are better than that of the IEX Pilot Brine, which could be due to the initial concentrations in the raw IEX Pilot Brine versus IEX Andijk III Brine:

- Chloride to NOM: \( \frac{2700 \text{ g}}{\text{L}} \text{Cl}^- : \frac{1 \text{ g}}{\text{L}} \text{TOC} \)
- Chloride to sulfate: \( \frac{83 \text{ g}}{\text{L}} \text{Cl}^- : \frac{1 \text{ g}}{\text{L}} \text{SO}_4^{2-} \)

*Table 7: Ion Concentration of Andijk III Brine and Concentrate at 90 mS/cm*

<table>
<thead>
<tr>
<th></th>
<th>Chloride g/L</th>
<th>Bicarbonate g/L</th>
<th>Sodium g/L</th>
<th>NOM mg/L</th>
<th>Sulfate g/L</th>
<th>Conductivity mS/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Diluate Feed</td>
<td>5</td>
<td>3</td>
<td>9</td>
<td>333</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>Concentrate Final</td>
<td>33</td>
<td>11</td>
<td>28</td>
<td>12</td>
<td>0.4</td>
<td>84</td>
</tr>
</tbody>
</table>

4.1.5 Mono-Selective Membrane Evaluation

After 870 hours of pilot operation, the mono-selective membranes were analyzed by the membrane supplier. A visual stack inspection, electrical resistance, burst strength, and hydraulic permeability were tested on the used membranes and compared to new ones. Once the membranes were evaluated, the stack was reassembled, or “refurbished”.

Table 8 presents data collected during the stack evaluation (demineralization test) with respect to leakage, pressure drop, and voltage on the stack before and after refurbishment. These data were compared to the performance at stack build-up with new membranes (December 1, 2015). All three tests show zero external and internal leakage; voltage decreased slightly between
the new and used membranes, and current efficiency was acceptable for all experiments. Pressure in the stack before the evaluation was double that of the other two experiments, which was due to the build-up of ion-exchange resins at the inlet. Once the resins were manually removed during the visual inspection, the pressure was restored to 0.4 bar. This data supports the data collected during the demineralization tests at PWNT (Section 4.1.3).

<table>
<thead>
<tr>
<th>Date</th>
<th>External leakage</th>
<th>Internal leakage</th>
<th>ΔP @30 °C (bar)</th>
<th>U(V)</th>
<th>T(°C)</th>
<th>Ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>01/12/2015</td>
<td>0</td>
<td>0</td>
<td>0.45 (25°C)</td>
<td>44.8</td>
<td>23.8</td>
<td>82%</td>
</tr>
<tr>
<td>18/07/2016</td>
<td>0</td>
<td>0</td>
<td>0.95</td>
<td>29.1</td>
<td>31.0</td>
<td>81%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30.1</td>
<td>33.0</td>
<td>82%</td>
</tr>
<tr>
<td>19/07/2016</td>
<td>0</td>
<td>0</td>
<td>0.40</td>
<td>30.3</td>
<td>27.0</td>
<td>79%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>33.4</td>
<td>30.0</td>
<td>76%</td>
</tr>
</tbody>
</table>

Visual inspection of the stack was performed after the demineralization test (18/07/2016) to observe any physical defects, fouling, or organic matter deposition on the membranes. Figure 63 displays the physical state of a cationic and anionic membrane. This inspection showed no physical defects, fouling, and deposition of organic matter on the surface of the membranes. However, the distributors contained quite a few ion-exchange resins which got stuck during the operation as shown in Figure 64. This blockage is likely the cause of the high pressure drop in the 18/07/2016 demineralization experiment. Cell 25 was extracted for further testing on the mechanical properties, and replaced with new membranes.
The final membrane analysis tested the electrical resistance, burst strength, and hydraulic permeability of the anion and cation membrane removed from the used stack (cell 25). Figure 65
presents the results of the electrical resistance experiments. Electrical resistance was measured using 0.5 N NaCl and 0.5 N Na₂SO₄ for the anion membrane and 0.5 N NaCl for the cation membrane to observe monovalent and divalent ion selectivity. Acceptable error in the electrical resistance experiments was estimated to be 5%. Electrical resistance of anion-exchange membranes increased by 15% with respect to monovalent ions, and by 100% for divalent ions. A high resistance for divalent ions is desired since the mono-selective membrane target the passage of monovalent ions rather than multivalent ions. Electrical resistance of the cation-exchange membranes was within a 5% change. Therefore, these results suggest ion selectivity did not worsen over 870 hours of operation.

![Figure 65: Electrical Resistance of Anion- and Cation-Exchange Membranes (Eurodia Membrane Evaluation Report 2016)](image)

Table 9 displays the results of the burst strength and hydraulic permeability experiments on new and used membranes. Burst strength of both anion- and cation-exchange membranes are within acceptable uncertainty (5%), which indicates the mechanical properties are likely the same.
Hydraulic permeability of anion- and cation-exchange membranes was zero for new and used samples, which indicates there is no non-selective transfer of water through the membranes.

Table 9: Burst Strength and Hydraulic Permeability (Eurodia Membrane Evaluation 2016)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Burst strength (MPa)</th>
<th>Hydraulic permeability (ml/h.m².0,1 MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>New</td>
<td>0.200</td>
<td>0</td>
</tr>
<tr>
<td>Used 870h</td>
<td>0.190</td>
<td>0</td>
</tr>
<tr>
<td>CMXsb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>New</td>
<td>0.400</td>
<td>0</td>
</tr>
<tr>
<td>Used 870h</td>
<td>0.390</td>
<td>0</td>
</tr>
</tbody>
</table>

The membrane evaluation provided positive results on the condition of the membranes after 870 hours of operation, such that the stack and membranes are in very good condition after 870 hours of operation. Key points concluded from this analysis include:

- Membranes were in good condition,
  - No physical defects
  - No organic deposition
  - No fouling
- Electrical resistance did not decrease and was the same in both normal and EDR operation,
  - Electrical resistance of NaCl for cation-exchange membranes was roughly the same
  - Electrical resistance of NaCl for anion-exchange membranes slightly increase, which is normal
  - Electrical resistance of Na₂SO₄ nearly doubled, suggesting ion selectivity towards monovalent ion was not damaged and even increased,
- Mechanical properties did not change after 870 hours of operation, and
Hydraulic permeability did not change after 870 hours of operation.

4.2. Non-Selective Membrane Batch Experiment Results

4.2.1 Determination of Concentrate Conductivity Limit

The non-selective electrodialysis stack (EDNS) is used after the mono-selective stage to treat the brine which was previously desalinated to 14-19 mS/cm with mono-selective membranes to remove sodium chloride and bicarbonate. In this process, sulfate (SO$_4^{2-}$) will be separated from natural organic matter (NOM). EDNS stack was run in fourteen sequential 5-hr batches to determine the performance of separation with respect to increasing concentrate conductivity. The initial concentrate stream was made of 60 L of reverse osmosis water and dissolved sodium sulfate up to 10 mS/cm. The concentrate solution was recycled for all fourteen batch experiments, only draining to the initial volume of 60 L at the beginning of each experiment. The diluate stream is the brine product from the mono-selective stage with a volume of 190L; it is disposed of and renewed after each batch.

Figure 66 illustrates concentrate and diluate conductivity, current density, and concentration of NOM (measured as TOC) and sulfate. On the lower window, the concentrate conductivity gradually increases for the first 30 hours of operation then remains stable at around 80 mS/cm. The diluate conductivity decreases on average from 17 to $\leq$ 5 mS/cm, which is constant across all fourteen batches. This, together with a consistent current density is an indication that ion transfer is occurring through the membranes. After 25 hrs, samples of the concentrate were taken and analyzed for NOM and sulfate to explain the conductivity plateau. These analytical results, displayed in the two windows above, also show that neither sulfate nor NOM concentrations were increasing in the concentrate after the 8$^{th}$ consecutive batch.
As previously stated, the purpose of the EDNS stage is to separate $\text{SO}_4^{2-}$ from NOM in the monovalent ion-free pilot brine. Therefore, the goal is to minimize NOM passage across the membranes. Unfortunately, the more concentrated $\text{SO}_4^{2-}$ is in the concentrate stream, more NOM passes through the membrane due to higher osmotic pressure. Figure 66 shows the concentration of NOM and sulfate at the end of each batch run. This data suggests that separation of sulfate from NOM in EDNS is more difficult than the separation of $\text{Cl}^-$ from NOM in the mono-selective stage. For instance, the ratio of $\text{Cl}^-$ to NOM in the mono-selective treatment is 3000:1, whereas the ratio of $\text{SO}_4^{2-}$ to NOM in EDNS is 300:1.

![Non-Selective Membrane Conditions](image)

*Figure 66: EDNS Conductivity, Current Density, Sulfate Passage, and NOM Passage*

Figure 67 and Figure 68 display sulfate and NOM concentration in EDNS concentrate between 20 and 65 hours of operation. Sulfate concentration increases from 35 to 40 hours, and then seems to plateau with some variation until the end of the experiment. These data are adjusted with respect to water passage, therefore it is likely sulfate concentration reaches steady state at
approximately 80 mS/cm. NOM concentration over these 40 hours seems to be quite variable between each trial, increasing and decreasing in a similar pattern of sulfate concentration. These data indicate that NOM passage is related to sulfate passage, i.e. the more sulfate that is recovered, NOM transport is also increased across the membrane.

Figure 67: Sulfate Concentration in EDNS Concentrate

Figure 68: NOM Concentration in EDNS Concentrate
Figure 69 puts in perspective the increase of concentrate conductivity and decrease of diluate conductivity during each batch run. In Figure 70 the average rates of conductivity change per hour of operation are calculated and displayed. From these two figures it becomes clear the condition of ion passage worsens overtime. On March 3rd concentrate displayed an increase of 21% of its conductivity value and diluate a decrease of 14%. The difference between these two percentages is explained by the difference in volume of the two liquids, but it is assumed all of the ions removed from the diluate ends up in the concentrate. While the load of ions being transferred from the diluate per batch remains constant (Figure 69), the rate of transfer decreases (Figure 70) which is expected as the concentration gradient (osmotic pressure) increases between the two solutions. On the concentrate side, it seems that ions passage is decreased batch after batch, in contradiction with previous statement, and with it its transfer rate. The first batch is different than the rest because the concentrate conductivity and sulfate concentration were at their lowest values indicating osmotic pressure and stack resistance is lower than the subsequent trials.

![Change in Conductivity](image)

*Figure 69: Change in conductivity of concentrate and diluate*
Measurements on the volume variation were taken and displayed in Figure 71. The perfect match between the increase in concentrate volume and the decrease in diluate volume for each batch run confirms the permeation of water from the diluate to the concentrate across the EDNS membranes. Two phenomena for water passage can be explained by:

- Resistance due to increased osmosis force
- Water transport due to electro-osmosis

It is in fact a well-known phenomenon that ions surround themselves with polar molecules of water due to their charges, which is explained by electro-osmosis (Sata 2007, Pronk et al 2006). During the ED process, they permeate in hydrated form bringing H₂O with them. This phenomenon was hardly observed in in the first stage of ED, because chloride and bicarbonate are not very hydrated ions. However, sulfate carries 8 to 10 molecules of water, which explains the higher water transport due to electro-osmosis. Additionally, water passage increases with concentrate conductivity due to a higher osmotic pressure across the membranes. In the first three
batch runs (March 3, 15, and 16, totaling 15 hours), there was approximately 10 L of water passage because the concentration gradient between the two solutions was less that the subsequent trials. During the fourth trial (and thereafter), 15 L of water was transported across the membranes due to a larger concentration gradient. The fourth batch run was completed at 20 hours of operation, at which the concentrate conductivity approaches its limit of 80 mS/cm (Figure 66). Increase in osmotic force and consequently increase in stack resistance similarly explains the slowdown of both diluate and concentrate conductivity rates in Figure 70. The concepts of electro-osmosis and osmotic pressure are further explained in Section 2.1.1.

![Water Passage Chart](image)

**Figure 71: Volume change (L) due to water passage across membranes**

4.2.2 **Adjustment of pH to Improve Separation of Sulfate and NOM**

The purpose of this experiment was to determine if altering the pH of the diluate would improve the separation of sulfate from NOM. From previous operation with non-selective membranes (Section 2.3.2, Lebon et al 2014), a limit to sodium sulfate passage was found. As a result, final conductivity of the brine cannot be reduced past 5 mS/cm, limiting the application possibilities of humic substances for agriculture. One hypothesis was possible interaction between
the NOM and sodium sulfate hindering its passage due to slow moving NOM through the membrane or fouling on the membrane surface (Lindstrand et al 2000). Under the effect of lowering the pH below isoelectric point, net charges on NOM groups are expected to change breaking electrostatic interaction. This experiment looks at optimizing the organic/inorganic separation by pH adjustments. It included two trials:

- Diluate with normal pH (approximately pH 9)
- Diluate with low pH, adjusted with 1.3 L 10% HCl (titration in Appendix I) (approximately pH 5)

Table 10 provides a direct comparison of NOM and sulfate passage with and without pH adjustment. This data suggests that there was no difference between treating the diluate with a normal pH to that of the low pH:

- There is a slightly higher passage of sulfate with the adjusted pH – 70% instead of 65%,
  This is however most likely due to higher initial concentration than to effect of pH unbounding NOM and ions; and
- There is a slightly higher passage of NOM – could be the NOMs breaking down under the effect of pH, allowing passage of the smaller pieces.

Overall no improvement noticed by lowering pH. This experiment also didn’t prove the existence of bounds between organics and inorganics nor that NOM hinders the passage of sodium sulfate.
Table 10: NOM and Sulfate Passage, EDNS pH Adjustment Experiment

<table>
<thead>
<tr>
<th></th>
<th>Volume (L)</th>
<th>NOM mg/L</th>
<th>Adjusted mg/L</th>
<th>Change</th>
<th>% NOM Passage</th>
<th>Sulfate g/L</th>
<th>Adjusted g/L</th>
<th>Change</th>
<th>% SO₄²⁻ Passage</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 9</td>
<td>Initial Diluate</td>
<td>200</td>
<td>266</td>
<td>266</td>
<td>23.6</td>
<td>8.8%</td>
<td>3.4</td>
<td>3.4</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>Final Diluate</td>
<td>195</td>
<td>249</td>
<td>243</td>
<td></td>
<td>1.1</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Initial Concentrate</td>
<td>60</td>
<td>7.0</td>
<td>7.0</td>
<td>25.7</td>
<td>2.9%</td>
<td>4.2</td>
<td>4.2</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>Final Concentrate</td>
<td>65</td>
<td>30.2</td>
<td>32.7</td>
<td></td>
<td>10.2</td>
<td>11.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = 5</td>
<td>Initial Diluate</td>
<td>200</td>
<td>312</td>
<td>312</td>
<td>30.0</td>
<td>9.6%</td>
<td>4.2</td>
<td>4.2</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>Final Diluate</td>
<td>195</td>
<td>289</td>
<td>282</td>
<td></td>
<td>1.2</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Initial Concentrate</td>
<td>60</td>
<td>5.8</td>
<td>5.8</td>
<td>43.1</td>
<td>4.1%</td>
<td>3.5</td>
<td>3.5</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>Final Concentrate</td>
<td>65</td>
<td>45.1</td>
<td>48.9</td>
<td></td>
<td>12.1</td>
<td>13.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.3. Bench-Scale Test Results

The bench-scale experiments included comparing the impact of brine type, spacer size, and pretreatment (filtration) of brine on spacer clogging over a 2-day period. A validation test was conducted to compare the results to the standard sized particles and spacer. Parameters compared include: pressure, particle sizes in the influent and effluent, biological growth at the inlet and outlet on membrane and spacer, and SEM images (some experiments).

4.3.1 Validation Test with Standard-Sized Particles

The validation test was conducted as a control measure for this bench-scale experiment to observe the retention of particles over time. Figure 72 displays the pressure data over the 2-day experiment using RO water, standard sized particles (Duke Standards, NIST Traceable Polymer, 1.5x10⁸ particles with a diameter of 5.021 µm +/- 0.041 µm), and a standard sized spacer (450 µm). The pressure increased from 0.037 to 0.099 bar. Over the length of the experiment, the total pressure increase was approximately 0.062 bar. Pressure data is recorded every second of the experiment. Therefore, a range of pressures is observed, especially towards the end of the
experiment. The larger range in the data can be attributed to the nature of the feed pump – peristaltic pump pulse creates flow, therefore, as the spacer gets clogged, the “pulses” get larger. The flow decreased from 3.34 L/h to 3.29 L/h at the end of the experiment. The decreased flow was due to particle retention on the spacer.

Figure 73 shows average particle load of the validation solution with RO water and standard-sized particles at the inlet and outlet of the spacer unit. Average particle load is measured by grouping particle diameters in to categories ranging from 1 µm to 15 µm. The 15 µm category incorporates all particles larger than 15 µm as well. This experiment was conducted with 3 L of RO water and 1.5x10^8 particles of 5 µm, therefore it was expected to see 50 vol ppb of 5 µm particles. Figure 73 shows the average particle load of 5 µm was approximately 100 vol ppb which is double the expected load. Additionally, average particle load data suggests there is a significant load of particles sized larger than 5 µm. There are a few possibilities which may have caused this discrepancy:

- Particle counter was not calibrated correctly,
- Experiment was not conducted in a “particle-free” environment therefore results in variation in the data,
- There was some contamination in the experiment, or
- Particles agglomerated together.

It is more likely that there was contamination in the cell unit (from previous experiments and not having a particle-free environment) because biomass particles were observed at the inlet of the cell unit at the end of the experiment (Figure 74). The particle counter was located at KWR, and therefore is more likely to be properly calibrated due to the high demand of the equipment.
Figure 73 also shows that some amount of each size particle can be retained in the unit but retention increases significantly above 7 µm. Furthermore, 10 and 15 µm sizes are retained by over 90%.

**Figure 72: Pressure, Bench-Scale Unit Validation Test with Standard-Sized Particles**

**Figure 73: Particle Load, Bench-Scale Unit Validation Test with Standard-Sized Particles**
4.3.2  **Comparison of Spacer Size (450 and 750 µm)**

Two electrodialysis spacer sizes (450 and 750 µm) were compared to observe the impact of using a larger spacer versus a smaller spacer.

4.3.2.1  **Pilot IEX brine and standard spacer, 450 µm**

Figure 75 displays the pressure data when using the IEX Pilot Brine and standard spacer size (450 µm). The pressure increases rapidly from 0.054 bar to approximately 0.35 bar during the first 5 hours due to particle buildup at the inlet of the cell, which required the pump speed to be reduced and therefore the pressure drops to about 0.25 bar. The pressure stayed relatively constant until the last few hours of the experiment when it increased to 0.30 bar. Over the length of the experiment, the total pressure increase was approximately 0.25 bar. The flow decreased from 5.34 L/h to 1.54 L/h at the end of the experiment. The decreased flow was observed even before the pump speed was reduced, which was reflected due to the spacer clogging and pressure increase at the head of the unit.
Figure 76 shows average particle load of the IEX Pilot Brine at the inlet and outlet of the spacer unit. The IEX Pilot Brine mainly consists of particles of 4 – 15 µm in diameter (90% of particles). Average particle load data also shows that particles of 1-5 µm in diameter pass through the spacer, whereas particles larger than 5 µm in diameter are retained in the cell unit.

Figure 75: Pressure, Bench-Scale Unit with Standard Spacer (450 µm) and Pilot Brine

Figure 76: Particle Load, Bench-Scale Unit with Standard Spacer (450 µm) and Pilot Brine
Figure 77 and Table 12 (Section 4.3.5) indicate that part of the pressure increase and particle retention is likely due to the build-up of biomass at the head of the SFS. Figure 77 also shows a gradient of the particles and biomass present, where there is a higher concentration of solids at the inlet and it gradually decreases towards the outlet of the SFS.

Figure 77: IEX Pilot Brine, 450 µm Spacer, Build-Up of Particles and Biomass at Inlet

4.3.2.2 Pilot IEX Brine and Large Spacer, 750 µm

Figure 78 shows the pressure at the inlet of the cell unit over 50 hours of operation with a 750 µm spacer and IEX Pilot Brine. The pressure increases from 0.001 bar to 0.023 bar, which results in a total pressure increase of 0.022 bar. Here, pressure is quite low compared to that of the 450 µm spacer which is likely due to less retention of particles over the length of the cell unit.

Figure 79 displays the average particle load data in the influent and effluent of the cell unit with IEX Pilot Brine and 750 µm spacer. Similar to the trial with 450 µm spacer and IEX Pilot Brine, brine mainly consists of particles of 4 – 15 µm in diameter (90% of particles). Average particle load data also shows that particles of 1-5 µm in diameter pass through the spacer, whereas particles larger than 5 µm in diameter are retained in the cell unit.
Figure 78: Pressure, Bench-Scale Unit with Large Spacer (750 µm) and Pilot Brine

Figure 79: Particle Load, Bench-Scale Unit with Large Spacer (750 µm) and Pilot Brine
4.3.2.3 Spacer Size Comparison, Pressure and Particle Load

Figure 80 compares the pressure data for the cell operation with 450 µm spacer and 750 µm spacer using IEX Pilot Brine. The 450 µm spacer show a high increase of pressure during the 2-day experiment (0.25 bar), such that the pump speed needed to be reduced to prevent the hose from bursting, whereas the 750 µm spacer experienced significantly less pressure increase (0.022 bar).

Figure 81 compares the amount of particle retention on the 450 µm and 750 µm spacer with IEX Pilot Brine. The 450 µm spacer retains (120 ppb) more than the 750 µm spacer. The biggest contributor is the 15 µm particles, where there are 100 ppb more retained on using the 450 µm spacer versus the 750 µm spacer. The decreased amount of particle retention for the 750 µm spacer contributes to the significantly lower pressure increase over time.

![Pressure, Spacer Comparison: 450 and 750 um](image)

*Figure 80: Pressure Comparison, Bench-Scale Unit with 450 µm and 750 µm Spacer*
4.3.3 Filtered Brine Comparison

Two types of pretreatment (10-micron and 50-micron filters) of IEX Pilot Brine are discussed in this section to observe the impact on the standard-sized spacer (450 µm).

4.3.3.1 Pilot IEX Brine Filtered with 10-micron Filter and Standard Spacer, 450 µm

Figure 82 presents the pressure data collected on the cell operation with IEX Pilot Brine pretreated with a 10-micron filter. Over the duration of this experiment, the pressure did not increase, but rather fluctuated between 0.060 to 0.050 bar. The flow slightly decreased from 5.5 to 5.35 L/h during the experiment, however this could be due to particle clogging the filter before entering the bench-scale unit. Unfortunately, the original file for particle load data for this experiment was lost, however, Figure 87 shows the comparison of particles retained in SFS.
Figure 82: Pressure, Bench-Scale Unit with Standard Spacer and IEX Pilot Brine Pretreated with 10-Micron Filter

4.3.3.2 Pilot IEX Brine Filtered with 50-micron filter and Standard Spacer, 450 µm

Figure 83 presents the pressure data collected on the cell operation with IEX Pilot Brine pretreated with a 50-micron filter. Over the duration of this experiment, the pressure slightly increased from 0.065 to 0.138 bar. The pressure stayed relatively constant for the majority of the experiment, then spiked after 32 hours which can likely be attributed to a larger particle blocking part of the influent channel. The flow slightly decreased from 5.85 to 5.35 L/h during the experiment, however this could be due to particle clogging the filter before entering the bench-scale unit or particle clogging on the spacer.

Figure 84 presents the average particle load data of the influent and effluent of the cell unit with IEX Pilot Brine pretreated with a 50-micron filter. The majority of the particles in the influent are sized 5 – 15 µm in diameter (85%). Average particle load data also shows that 20% of particles
pass through the spacer, whereas the remaining 80% of particles are retained on the spacer. The total particle load of the 50-micron filtered IEX Pilot Brine is significantly lower than that of the unfiltered IEX Pilot Brine, approximately 80% less particles. As expected, the average particle load data shows a much lower particle load for the treated brine versus untreated brine.

Figure 85 and Table 12 (Section 4.3.5) indicate that part of the pressure increase and particle retention is likely due to the build-up of biomass at the head of the SFS. Comparing Figure 77, Figure 85, and data in Table 12, filtering the IEX Pilot Brine with a 50-micron filter decreased the biomass and particle accumulation at the inlet of the SFS.

![Pre-Treatment with 50-Micron Filter](image)

**Figure 83: Pressure, Bench-Scale Unit with Standard (450 µm) and Pilot Brine Pre-Treated with 50-Micron Filter**
4.3.3.3 Pre-Treatment Comparison

Figure 86 compares the pressure data of the IEX Pilot Brine treated with a 10-micron filter and a 50-micron filter. The experiment with a 10-micron filter showed a negligible pressure
increase, where the 50-micron filtered brine showed a pressure increase of 0.073 bar. Compared to the pressure increase using unfiltered brine (0.25 bar), pressure increase was reduced with both methods of brine pretreatment. The 10-micron filter does not seem to improve pressure when compared to the 50-micron filter, and will likely clog much faster than the 50-micron filter. Therefore, if pretreatment of the brine was chosen, the 50-micron filter should be sufficient to reduce spacer clogging.

Figure 87 compares the amount of particle retention on the 450 µm spacer with IEX Pilot Brine pre-treated with a 10- or 50-micron filter. Pre-treating with a 10-micron filter shows less particle retention, which makes sense because there should be less particles present in the influent when compared to that of the brine filtered with the 50-micron filter. Less particle retention in the IEX Pilot Brine pre-treated with the 10-micron filter results in less pressure increase over time. The biggest contributors are the 7-15 µm particles.
Figure 86: Pressure Comparison, Bench-Scale Unit with Standard (450 µm) and Pilot Brine Pre-Treated with and 10- or 50-Micron Filter

Figure 87: Particle Load Comparison, Bench-Scale Unit with Standard (450 µm) and Pilot Brine Pre-Treated with and 10- or 50-Micron Filter
4.3.4 Comparison of Brine Type

Three brine types (IEX Pilot Brine, Andijk III Brine, and Denitrified Brine) were compared to observe the impact on the standard-sized spacer (450 µm) on pressure and particle retention. The IEX Pilot Brine pressure and particle loading data is discussed in the previous section. Data collected on IEX Andijk III Brine and IEX Denitrified Brine are discussed below.

4.3.4.1 Andijk III IEX Brine and Standard Spacer, 450 µm

Figure 88 presents the pressure data collected on the cell operation with IEX Andijk III Brine. Over the duration of the experiment, the pressure increased from 0.042 to 0.25 bar. The flow slightly decreased from 3.48 to 3.12 L/h during the experiment, which is likely due to particle clogging on the spacer. The pump speed was reduced for this experiment to reduce the risk of the hose bursting.

Figure 89 displays the average particle load data in the influent and effluent of the bench-scale unit with IEX Andijk III Brine and standard spacer (450 µm). Similar to the trial with 450 µm spacer and IEX Pilot Brine, brine mainly consists of particles of 4 – 15 µm in diameter (90% of particles). Average particle load data shows that particles of 1-3 µm in diameter pass through the spacer, whereas particles larger than 3 µm in diameter are retained in the cell unit. Particle retention is likely causing the pressure increase over time.

Figure 90, Figure 91, and Table 12 (Section 4.3.5) indicate that part of the pressure increase and particle retention is likely due to the build-up of biomass at the head of the SFS. In this case, there is also a significant amount of resins built up at the inlet of the SFS. Additionally, the SFS clogging by resins caused a channeling through the cell, which resulting in air bubbles towards the outlet of the SFS. The ATP data in Table 12 suggest that there is more biomass when using the
IEX Andijk III Brine when compared to the IEX Pilot Brine. However, the differences could be due to variation between test and may not be significant.

*Figure 88: Pressure, Bench-Scale Unit with Standard (450 µm) and Andijk III Brine*

*Figure 89: Particle Load, Bench-Scale Unit with Standard (450 µm) and Andijk III Brine*
4.3.4.2 Denitrified (DNF) IEX Brine and Standard Spacer, 450 µm

Figure 92 presents the pressure data collected on the cell operation with IEX Denitrified Brine. Over the duration of this experiment, the pressure increased from 0.029 to 0.268 bar. The flow began at 3.3 and did not decrease until the pump speed had to be reduced due to the high increase of pressure after 32 hours of running the bench-scale unit. The data after the speed was
reduced was omitted from this graph because it cannot be compared. The high pressure increase is explained in Figure 93.

Figure 93 presents the average particle load data in the influent and effluent of the bench-scale unit with IEX Denitrified Brine and standard-sized spacer (450 µm). This data shows that the majority of the particles are 15 µm or greater in diameter. In this experiment, the particle load is much higher than the previous experiments by an order of magnitude; total particle load exceeds 6000 vol ppb. Average particle load data shows that particles of 1-10 µm in diameter pass through the spacer, whereas particles 15 µm or larger in diameter are retained in the cell unit. However, the data also suggests there are more particles in the effluent than in the influent for 2-10 µm particles, which means particles are building up throughout the length of the unit and are being pushed out as more particles enter. It is possible that particles smaller than 15 µm in diameter are being retained on the spacer, however, this is not reflected in the data because of the surplus of particle leaving the unit. Particle retention (15 µm in diameter) is likely causing the pressure increase over time.

Figure 94, Figure 95, and Table 12 (Section 4.3.5) indicate that a majority of pressure increase and particle retention is likely due to the build-up of biomass at the head of the SFS. In this case, the nature of the brine is different than the other trials; microbes are used in the denitrification process which are still present during this SFS experiment. The ATP data in Table 12 suggest that there is approximately 30x more biomass when using the IEX DNF Brine on at the inlet and outlet when compared to the IEX Pilot Brine and Andijk III Brine.
Figure 92: Pressure, Bench-Scale Unit with Standard (450 µm) and DNF Brine

Figure 93: Particle Load, Bench-Scale Unit with Standard (450 µm) and DNF Brine
Figure 94: IEX DNF Brine, 450 µm Spacer; Particles and Biomass at Inlet

Figure 95: IEX DNF Brine, 450 µm Spacer; Particles and Biomass Inlet, Top from SFS removed

4.3.4.3 Brine Type Comparison

Figure 96 compares the pressure data of each experiment with IEX Pilot Brine, Andijk III Brine and Denitrified Brine. Table 16 shows the pressure increase during each bench-scale experiment with the three types of brine. IEX Pilot Brine and Denitrified brine have the two highest pressure increases which make sense because IEX Andijk III brine is less concentrated. It is likely that the IEX Denitrified Brine has less pressure increase because the particles moving through the
spacers is biological rather than solid particles. Therefore, the particles have more flexibility to move around the spacer, which is why effluent particle load is greater than the influent.

Table 11: Pressure Increase for each IEX Brine Type

<table>
<thead>
<tr>
<th>IEX Brine Type</th>
<th>Pressure Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pilot</td>
<td>0.245 bar</td>
</tr>
<tr>
<td>Andijk III</td>
<td>0.226 bar</td>
</tr>
<tr>
<td>Denitrified (DNF)</td>
<td>0.239 bar</td>
</tr>
</tbody>
</table>

Figure 97 compares the average particle retention during the three experiments with standard spacers. The IEX Denitrified Brine has significantly more particles retained in the cell than the other two brines, and it shows that the smaller particles build up in the unit and exit in higher quantities. The average particle load between the IEX Pilot and Andijk III Brine slightly different, with more particles retained in the Andijk III Brine. While the pressure increase was less over the duration of the 2-day experiment, this particle load data was collected after running cell for an additional day. Over the full length of the experiment, the pressure increased 0.248 bar, which is higher than that of the IEX Pilot Brine experiment and explains the increased particle retention.
Figure 96: Pressure Comparison, Bench-Scale Unit with Standard (450 µm) and IEX Pilot, Andijk III, or DNF Brine
4.3.5 **Bench-Scale Experiment ATP Results**

During the 2-day bench-scale study, ATP was measured to compare biological growth on the spacer and membranes under each condition described. Table 12 shows the results from each experiment, except for the 10-micron filtered IEX Pilot Brine due to complications with the measurement. It is clear the denitrified brine (DNF) has the most growth. This is because the DNF brine is treated with a biological process, and therefore, biological matter is still present in the brine during this experiment. From these results, it is also clear that the spacer contains more ATP than the membrane, which makes sense because biological material can get stuck in the lattice.
structure of the spacer, whereas the membrane is a flat surface which sits underneath the spacer. These results lead to the question of whether or not there is a potential of biofouling in the electrodialysis system.

Table 12: ATP Measurements for Each Bench-Scale SFS Experiment

<table>
<thead>
<tr>
<th>Spacer Size (µm)</th>
<th>Brine Type</th>
<th>ATP Inlet (pg/cm²)</th>
<th>ATP Outlet (pg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Membrane</td>
<td>Spacer</td>
</tr>
<tr>
<td>450</td>
<td>Pilot</td>
<td>1,512</td>
<td>10,874</td>
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<tr>
<td>750</td>
<td>Pilot</td>
<td>17,651</td>
<td>35,491</td>
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<tr>
<td>450</td>
<td>Andijk III</td>
<td>1,180</td>
<td>39,363</td>
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<tr>
<td>450</td>
<td>DNF</td>
<td>80,935</td>
<td>1,132,829</td>
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<tr>
<td>450</td>
<td>Filtered Pilot (10-micron)</td>
<td>2,284</td>
<td>12,068</td>
</tr>
<tr>
<td>450</td>
<td>Filtered Pilot (50-micron)</td>
<td>Error in Sampling Method</td>
<td></td>
</tr>
</tbody>
</table>

4.3.6 SEM Images and EDS Analysis

4.3.6.1. Standard Spacer Size (450 µm) with IEX Pilot Brine

Figure 98 - Figure 101 present the scanning electron microscopy (SEM) and energy dispersive atomic X-ray spectrometry (EDX) analyses of the used 450 µm spacer to analyze the constituents present on the spacer. Figure 98 shows a zoomed out SEM image of the 450 µm spacer. Figure 99 zooms into an area of dried brine situated on the lattice structure of the spacer. In order to classify the constituents forming the crystal shown in Figure 99 - Figure 101 use EDX to quantify the presence of carbon, oxygen, nitrogen, sodium, etc. Figure 100 shows the concentration of each elements by the density of the colored pixels. For example, the crystals shown in Figure 99 are made up of oxygen and sodium. Additionally, there is a significant amount of organics surrounding the crystals as indicated by the high concentration of carbon, oxygen, and nitrogen. Figure 101 confirms this by calculating the percent weight of each element: 45.6% of the constituents is carbon, 33% is oxygen, and 13.2% is nitrogen, and 5.4% is sodium.
Figure 98: SEM Image of Used 450 µm Spacer with IEX Pilot Brine, Inlet, x30

Figure 99: SEM Image of Used 450 µm Spacer with IEX Pilot Brine, Inlet, x3000
Figure 100: Presence of Elements, Used 450 µm Space, Inlet of Cell Unit
In addition to taking images of the spacer, the anion exchange membranes (AEM) were also analyzed under the microscope as shown in Figure 102. Figure 104 shows the EDX analysis to determine what is in Figure 102. Chloride and sodium are the two biggest components of the crystals in the microscopic image, whereas carbon and oxygen are next. Therefore, it can be concluded that the matter present is sodium chloride and organic matter. There is also some presence of sulfur and oxygen which suggests a small amount of sulfate as well. This is further supported in Figure 103, which concludes that 63% by weight is carbon, 13.3% by weight is oxygen, 9.6% is chloride, 4.6% is sodium, 0.6% is sulfur.
Figure 102: SEM Image, AEM of Used 450 µm Spacer with IEX Pilot Brine, Inlet, x500

Figure 103: EDX Analysis, AEM under Used 450 µm Spacer with IEX Pilot Brine, Inlet
Figure 104: EDX Analysis, AEM of Used 450 µm with IEX Pilot Brine, Inlet
4.3.6.2. Standard Spacer Size (450 µm) with IEX Pilot Brine, Pre-Treated with 10-Micron Filter

Figure 105 – Figure 107 present the SEM and EDX analysis of the used AEM to analyze the constituents present on the membrane. Figure 105 zooms into an area of dried brine situated on the used AEM. In order to classify the constituents forming the crystal shown in Figure 105, Figure 106 and Figure 107 use EDX to quantify the presence of carbon, oxygen, nitrogen, sodium, etc. Figure 106 shows the concentration of each element by the density of the colored pixels. For example, the crystals shown in Figure 105 are made up of chloride, oxygen, and sodium. Additionally, there is a significant amount of organics surrounding the crystals as indicated by the high concentration of carbon. Figure 107 confirms this by calculating the percent weight of each element: 70% of the constituents is carbon, 16.3% is oxygen, and 11.2% is chloride, and 1.8% is sodium.

Figure 105: SEM Image, Used AEM with 450 µm Spacer and IEX Pilot Brine Pretreated with 10-Micron Filter
Figure 106: EDX AEM, Used AEM with 450 µm Spacer and IEX Pilot Brine Pretreated with 10-
Micron Filter
Figure 107: EDX Analysis, Used AEM with 450 µm Spacer and IEX Pilot Brine Pretreated with 10-Micron Filter

4.3.6.3. Standard Spacer Size (450 µm) with IEX Denitrified Brine

Figure 108 – Figure 109 present the SEM and EDX analysis of the used AEM with IEX Denitrified Brine to analyze what constituents are present on the membrane. Figure 108 zooms into an area of dried brine situated on the used AEM. In order to classify the constituents forming the crystal shown in Figure 108, Figure 110 and Figure 109 use EDX to quantify the presence of carbon, oxygen, chloride, sodium, etc. Figure 110 shows the concentration of each element by the density of the colored pixels. For example, the crystals shown in Figure 108 are made up of sodium chloride, the object to the right of the crystals is sodium sulfate, and the matter along the top of the image is organic matter. Figure 109 confirms this by calculating the percent weight of each element: 62.1% of the constituents is carbon, 17.8% is oxygen, 15.5% is nitrogen, 2.6% is sodium, 0.8% is chloride, and 0.6% is sulfur.
Figure 108: SEM Image, Used AEM with IEX Denitrified Brine and 450 µm Spacer

Figure 109: EDX Analysis, Used AEM with IEX Denitrified Brine and 450 µm Spacer
Figure 110: EDX Analysis, Used AEM with IEX Denitrified Brine and 450 µm Spacer
4.3.6.4. Comparison of SEM and EDX Results

Figure 111 shows the Wt% from the four EDX analyses discussed above. The main constituents present are organic matter, represented by carbon, oxygen, and nitrogen; sodium chloride; and sodium sulfate.

Figure 111: Comparison of SEM and EDX Analysis

(a) EDX of debris on 450 µm Spacer, (b) EDX of AEM with 450 µm Spacer and IEX Pilot Brine,
(c) EDX of AEM with 450 µm Spacer and IEX DNF Brine, and (d) EDX of AEM with 450 µm Spacer and IEX Pilot Brine Pretreated with 10-micron Filter
4.4. **Biomass Production Potential (BPP) and Assimilable Organic Carbon (AOC) Results**

Two experiments can be conducted to measure the potential of biofouling: biomass production potential (BPP) and assimilable organic carbon (AOC) (discussed in Section 2.2.1.4). This section is a summary of the BPP and AOC results presented in a memorandum written by Vaudevire et al. 2016.

Three IEX brine qualities were tested for BPP: IEX Pilot Brine, Andijk III Brine, and DNF Brine; and one for AOC: desalinated IEX Andijk III Brine to < 5 mS/cm. Originally, all three brine qualities were going to be tested for AOC, but there were some complications with sampling. AOC measurements for IEX Andijk III Brine were conducted on desalinated IEX Andijk III brine and 100x diluted desalinated brine. Brine was diluted for the AOC experiment due to potential adverse effects of toxic components in the brine.

Table 13 presents the LC OCD results (measured by HWL), which shows that 98.2% of the carbon compounds are hydrophilic humic substances (HS) or carbon compounds of lower molecular weight.

### Table 13: Desalinated Andijk III Brine, LC OCD Results (HWL, Vaudevire et al. 2016)

<table>
<thead>
<tr>
<th>TOC (mg/L)</th>
<th>DOC (mg/L)</th>
<th>POC (mg/L)</th>
<th>HOC (mg/L)</th>
<th>CDOM (mg/L)</th>
<th>Polymers (mg/L)</th>
<th>DON (mg/L)</th>
<th>Aromaticity</th>
<th>Blocks (mg/L)</th>
<th>Neutrals (mg/L)</th>
<th>Acids (mg/L)</th>
<th>Inorg. Colloid (mg/L)</th>
<th>SUVA (L/mg/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>312</td>
<td>292</td>
<td>19</td>
<td>-14</td>
<td>306</td>
<td>4</td>
<td>1084</td>
<td>224</td>
<td>13710</td>
<td>4.23</td>
<td>657</td>
<td>62</td>
<td>16</td>
</tr>
<tr>
<td>100</td>
<td>93.8</td>
<td>6.2</td>
<td>-4.4</td>
<td>98.2</td>
<td>1.4</td>
<td>-</td>
<td>71.8</td>
<td>--</td>
<td>--</td>
<td>20.0</td>
<td>5.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Note: TOC, hence DOC may be too low.

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145
Table 14 presents the AOC results from undiluted and diluted desalinated IEX Andijk III Brine samples (measured by HWL). Both samples result in high AOC concentrations, i.e. 950 µg/L C for the undiluted sample and 1000 µg/L C for the diluted sample (roughly 0.3% of TOC). A shift in the species growth is also observed between the two samples: P17 shows primary growth in the undiluted sample, while NOX is more prevalent in the diluted sample. These data can be further explained in Figure 112.

**Table 14: Desalination IEX Andijk III Brine, AOC Results (HWL, Vaudevire et al 2016)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>NOX (µg/L C)</th>
<th>Standard Deviation</th>
<th>P17 (µg/L C)</th>
<th>Standard Deviation</th>
<th>AOC Total</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ed Treated</td>
<td>220</td>
<td>260</td>
<td>240</td>
<td>29.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ed Treated Diluted (X100)</td>
<td>7.5</td>
<td>8.3</td>
<td>7.9</td>
<td>0.59</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 112 shows NOX is the dominating species in both cases. In Figure 112a, NOX growth spikes during the first seven days of the experiment with undiluted IEX Andijk III Brine, then growth stops, at which time growth of P17 increases. However, in Figure 112b NOX growth is not inhibited, but P17 growth is inhibited due to competition with NOX. This suggests there is a toxic component to the desalinated brine which inhibits growth of NOX, whereas in the diluted sample the toxic component is not as harmful, so NOX flourishes and inhibits the growth of P17. These AOC data show higher than what is typically seen in drinking water in the Netherlands (Vrouwenvelder et al 2000), suggest there is a higher potential for biofouling with respect to the concentrations of bioavailable carbon. Additional information on the AOC results can be seen in Appendix J.

Table 15 presents the BPP data gathered by HWL. It is important to note that the IEX Andijk III Brine was only diluted 20x before measuring ATP concentrations, while it is suggested
that these brine samples need to be diluted 100x before testing for ATP. These results present a large amount error, and should not be considered when making conclusions. IEX Pilot Brine BPP results show a high concentration of biological growth. However, the IEX DNF Brine results in BPP measurements nearly 7.5 or 10x the concentrations of BP7 and BPC14, respectively, compared to that of the pilot brine. The magnified concentration of BP7 and BPC14 is likely due to left over acetate from the denitrification process for the IEX Pilot Brine. IEX Pilot and DNF Brine data represent extremely high BPP values when compared to typical values for BPP in drinking waters; BP7 ranges from 5 to 10.3 ng/L and BPC14 ranges from 68 to 152.3 mg/L.dATP (Vaudevire et al 2016).

Figure 112: Desalinated IEX Andijk III Brine, AOC Growth Curves (Vaudevire et al 2016)
(a) Desalinated IEX Andijk III Brine, undiluted; (b) Desalinated IEX Andijk III Brine, diluted
Table 15: IEX Brine BPP Results (Results reflect dilution factor)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dilution Factor</th>
<th>BP7 (ng/L)</th>
<th>Standard deviation</th>
<th>BPC14 (ng/L d.ATP)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>IEX Andijk 3 Brine</td>
<td>20</td>
<td>11,820</td>
<td>940</td>
<td>149,220</td>
<td>9,900</td>
</tr>
<tr>
<td>IEX Pilot DNF Inf</td>
<td>100</td>
<td>14,360</td>
<td>990</td>
<td>130,640</td>
<td>11,640</td>
</tr>
<tr>
<td>IEX Pilot DNF Eff</td>
<td>100</td>
<td>106,470</td>
<td>730</td>
<td>1,237,320</td>
<td>327,430</td>
</tr>
</tbody>
</table>

4.5. Discussion of Mono-Selective Membrane Pilot Test

4.5.1. Discussion of Batch Pilot Operation

These preliminary experiments using a batch mode of operation, constituted a first attempt to (1) follow changes of membrane performances in time; and (2) specifically observe the effect of the frequency of reversals to preserve operation stability under stable conditions. Membrane performance was measured in various ways, including net change in conductivity, average current density of each 5-hr trial, speed of ion transfer, and ion selectivity. Due to the daily RO rinsing partially cleaning the membranes, conclusions cannot be made from these data.

4.5.2. Discussion of Operational Data, F&B IEX Pilot Brine

Throughout the duration of the 210-hour experiment presented in Figure 37 and Figure 38, the specific settings under trial include:

- The frequency of reversal: once a day between 28 and 57 hours of operation; and twice a day between 57 and 115 hours, and

- The impact of CIP and RO rinses on restoring stable operations.

Unfortunately, however, it is difficult to apply a systematic approach and some operational mistakes and changes in brine quality can pollute the results because the pilot is a dynamic system.
With regard to reversals; the first period between 27 and 51 hr with one reversal a day displayed an important current density drop. After about 35 hours this current density drop caused a slowdown in ion transfer, which is visible by the flatter concentrate curve and longer diluate cycles. This indicates a non-optimum situation where pollutants are allowed to deposit on the membrane surface and increase membrane resistance. An increase in reversal frequency was then implemented. Because of operational reasons, a twice a day frequency couldn’t be implemented exactly every 12hr but every 8hr and 16hr instead. Once the system was reversed at 57 hours, the performance was slightly restored, as seen in the current density data. Generally, when observing the 12-hr EDR between 57 to 115 hours, performance is restored to a greater current density than that of the 24-hr EDR. Only between 57 and 64 hours, current density is low because the electrolyte conductivity fell below 20 mS/cm. Otherwise, the 12-hr EDR is able to maintain stable operation until 155 hr, when current density decreases at a steeper rate than previously observed in either of the 24-hr or 12-hr EDR. This suggests foulants on the membranes cannot be removed with a 12-hr EDR and brings up a second topic of importance in this discussion: the impact of CIPs and RO rinses. Decreasing performance could be attributed to the lack of a CIP for approximately 130 hours, a change of electrolyte at 116 hours, or increasing concentration of NOM and sulfate in the diluate.

Over 210 hours of operation, three CIPs were conducted and three RO water rinses. RO water rinses were performed for two reasons: the pilot unexpectedly shutdown overnight, or the operation needed to be shut down over the weekend less than a week after the previous CIP. CIPs should not be conducted often because studies have shown that high concentrations of NaOH and HCl can permanently damage the membranes (Ghalloussi et al 2013). Figure 37 and Figure 38
show the behavior of the pilot after each RO rinse and CIP. The RO rinse does not significantly improve the performance of the membranes, but rather keeps the performance consistent with the previous cycles. The CIPs conducted during the F&B operation with IEX Pilot Brine were completed at the beginning, middle, and end of the experiment. It was observed that the performance of the membranes significantly increased after 80 hours of operation after the CIP. About 70 hours after the first CIP, stack performance gradually decreases until the end of the experiment. While it is possible that the lack of CIP might contribute to the decreasing performance of the system, current density directly before the first CIP at 82 hours showed good performance.

A second possibility causing the decrease in current density between 155 and 210 hours of operation could be due to the change in electrolyte (sulfamic acid to sulfuric at 116 hours). After 2 days of using sulfuric acid instead of sulfamic acid, the performance of the membranes significantly decreased. The purpose of the electrolyte is to promote the flow of ions across the membranes. Therefore, characteristics of sulfamic acid make it more suitable (combination of nitrogen and sulfate) for an electrolyte over sulfuric acids however, this needs to be proven with additional research. While the use of sulfuric acid may decrease the performance over time, it is unlikely that it will cause deposition on the membranes and increase membrane resistance.

Finally, the impact of NOM and sulfate concentrations in the diluate are discussed later in this chapter. In conclusion, the performance of the ED pilot with IEX Pilot Brine was relatively stable up until 155 hours of operation. In further research, the cause of the decreasing performance after this time should be investigated as it could be due to lack of CIP, change of electrolyte, or concentration of NOM and sulfate in the diluate.
4.5.3. **Discussion of Operational Data of F&B, IEX Andijk III Brine**

Throughout the duration of the 386-hour experiment, diluate conductivity parameters, reversal frequency, and type of reversal were tested (normal EDR versus flash reversal). The diluate conductivity operational parameters were tested between 15 and 62 hours to determine the lower limit for diluate conductivity (14 mS/cm) under typical brine conditions. However, Figure 48 and Figure 49 show the low limit for diluate conductivity decreased to 12 mS/cm between 300 and 320 hours of operation due to varying conditions of the raw IEX Andijk III Brine. This can be confirmed by the range of conductivity for shorter diluate cycles and current density increasing between 282 and 300 hours until the lower limit of the diluate was decreased to 12 mS/cm. The IEX Andijk III Brine used was also visibly lighter suggesting there was less NOM in solution (Figure 113).

![Image](image-url)

*Figure 113: Varying IEX Andijk III Brine Conditions, Visual Observation*

Conducting an EDR every 12 hours during the first 150 hours of operation preserved membrane performance, however, a decrease in performance on one side of the membranes is observed. After the chemical CIP, the performance of the fouled side of the membrane is restored.
The fouling may have occurred during the diluate low conductivity limit experiment since this side of the membrane was used for a longer duration on this setting. Even with the decreased performance on one side, the 12-hr EDR provides stable performance of the membrane.

In addition to testing the 12-hr EDR, flash reversals were also tested during 5-min or 3-min intervals every 2 hours. During this time, full EDRs were also conducted to observe the impact of using both methods of reversal. The 5-min flash reversals every 2 hours were conducted from 153-228 and 320-386 hours, and the 3-min flash reversals every 2 hours were conducted from 228-320 hours. The 5-min flash reversal between 153 and 228 hours with periodic EDRs seemed to preserve membrane performance for the duration of the experiment with respect to both current density and rate of concentrate conductivity increase. Then, the 5-min flash reversal conducted later on in the experiment between 320 and 386 hours, showed good performance at first, but then rate of concentrate conductivity increase decreased between 340-373 hours of operation, which suggests fouling occurred. Rate of change in concentrate conductivity increased after the EDR, however, this was likely due to the change in IEX Andijk III conditions similar to the behavior seen in 282 to 300 hours. The 3-min flash reversals between 228 and 320 hours of operation resulted in relatively stable current density, but significantly lower rate of concentrate conductivity increase. The biggest challenge with the flash reversal is the result of increased salt passage back into the diluate from the concentrate, which is why a 3-min reversal was tested opposed to the 5-min reversal. However, the 3-min reversal is not long enough to remove charged deposition on the membranes.

These reversal experiments suggest that a 12-hr EDR is the best method for reversal. If a flash reversal is desired, this data shows that a 5-min flash reversal combined with 24-hr EDRs
might preserve membrane performance. However, this method should be further tested to confirm its applicability to this process.

Three CIPs were conducted during the 386-hour experiment and one RO rinse. As previously discussed, the RO rinse will only keep the performance consistent with the previous cycles; it will not improve performance. The first and third chemical CIPs significantly improved the performance of the membranes with respect to current density. The second chemical CIP did not seem to improve the current density much, however, this is likely due to the 3-minute flash reversal decreasing performance of the membranes.

The overall performance of the 386-hr F&B operation with IEX Andijk III Brine was relatively stable throughout the experiment specifically with weekly chemical CIPs and EDRs every 12-hr.

4.5.4. Discussion of Preventative Cleaning Strategy

The demineralization tests were performed after each chemical CIPs to measure the current performance of the membranes. Two types of CIPs were conducted: 0.1 N NaOH and 2.5% NaOH. The latter CIP has a higher concentration of NaOH, and can be more damaging to the membranes than the former. Figure 114 shows the average voltage and total demineralization after each CIP. After analyzing the demineralization tests of both CIP methods (M1,T1 and M2,T1), the CIP using 2.5% NaOH did not improve the system much more than the less intensive CIP did. Therefore, the subsequent CIPs were conducted with 0.1 NaOH.
The next step is to determine the optimum frequency of CIPs, to reduce permanent fouling but also to preserve the physical and mechanical properties of the membranes, as NaOH is known to cause membrane swelling. It is also important to consider the costs (financial and environmental) of conducting CIPs.

4.5.5. Discussion of NOM and Sulfate Passage

Measuring sulfate and NOM concentrations in the pilot system contribute to the first objective of this thesis: monitor operational parameters related to fouling over time (ion passage, speed of ion transfer, current density, conductivity, and quality of the concentrate at 90 mS/cm). During the F&B experiments with IEX Pilot and Andijk III Brines, ion passage and speed of transfer could not be determined because volume was not regularly measured with every sample. However, the quality of the concentrate at 90 mS/cm was measured during each experiment. Quality was measured as having low contamination of sulfate and NOM in the final product.
Table 16 presents chloride, sulfate, and NOM concentration in the raw diluate and final concentrate at 90 mS/cm during both F&B experiments. This data shows chloride is in excess when compared to sulfate and NOM for operation with both brines. For IEX Pilot Brine, there is a 1900:1 ratio of chloride to NOM and 60:1 ratio of chloride to sulfate in the final concentrate. For IEX Andijk III Brine, there is a 2700:1 ratio of chloride to NOM and 83:1 ratio of chloride to sulfate in the final concentrate. The higher ratio of chloride to NOM and sulfate shows higher quality of concentrate at 90 mS/cm, which is likely because there is less NOM and sulfate present in the raw IEX Andijk III Brine when compared to that of IEX Pilot Brine. This explains an important trade-off of electrodialysis to treat anion exchange regenerant: higher concentrations of multivalent ions in the diluate might result in higher concentrations in the resulting concentrate at 90 mS/cm. However, the decreased concentrate quality could be due to diluate contamination during the manual EDR. While this is a challenge, the concentrate in both cases shows high chloride to NOM and sulfate ratios.

Table 16: Comparison of IEX Pilot Brine and Andijk III Brine

<table>
<thead>
<tr>
<th></th>
<th>Chloride g/L</th>
<th>NOM mg/L</th>
<th>Cl⁻ : NOM</th>
<th>Sulfate g/L</th>
<th>Cl⁻ : SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw IEX Pilot Brine</td>
<td>11</td>
<td>510</td>
<td>--</td>
<td>7</td>
<td>--</td>
</tr>
<tr>
<td>Concentrate Final</td>
<td>36</td>
<td>19</td>
<td>1900:1</td>
<td>0.6</td>
<td>60:1</td>
</tr>
<tr>
<td>Raw IEX Andijk III Brine</td>
<td>5</td>
<td>333</td>
<td>--</td>
<td>5</td>
<td>--</td>
</tr>
<tr>
<td>Concentrate Final</td>
<td>33</td>
<td>12</td>
<td>2700:1</td>
<td>0.4</td>
<td>83:1</td>
</tr>
</tbody>
</table>

4.5.6. Overall Discussion of Pilot Operation

Mono-selective membranes were tested with continuous F&B operation using IEX Pilot Brine and IEX Andijk III Brine. During these experiments, operational data was monitored,
preventative CIPs were conducted to preserve membrane performance, NOM and sulfate concentrations were measured of the diluate and resulting concentrate, and at the end of these experiments the membranes were evaluated by the membranes provider. These experiments relate to the first and second objectives of this thesis Section 1.5.2.

The operational data for the continuous F&B operation with IEX Pilot Brine and IEX Andijk III Brine show overall stability in the process with respect to current density and increase of concentrate conductivity. On average the IEX Pilot Brine F&B operation yielded a higher current density than that of the IEX Andijk III Brine. This is likely due to the higher salt content in the IEX Pilot Brine versus the Andijk III Brine. However, there is a trade-off, such that heavier brine with higher salt content also contains more NOM and sulfate. Therefore, the quality of the resulting concentrate at 90 mS/cm is of a lower quality.

Towards the end of the F&B operation with IEX Pilot Brine, current density gradually decreases over time. While this could be attributed to the change of electrolyte, this could also be due to the increasing concentrations of NOM and sulfate in the diluate.

The overall resulting quality of concentrate at 90 mS/cm stayed relatively constant for both brine types. In each case, chloride was in excess when compared to NOM and sulfate. However, pilot operation with IEX Andijk III Brine yielded a concentrate of higher quality, such that the
chloride to NOM or sulfate ratios were higher than that of the IEX Pilot Brine. As previously mentioned, this could be due to the higher concentrations in the raw diluate of IEX Pilot Brine.

The membrane evaluation concluded that ion selectivity did not decrease over time. This report also concluded that there are no physical or mechanical defects after 870 hours of pilot operation.

During the full 596 hours of F&B pilot operation with IEX Pilot Brine and IEX Andijk III Brine, a variety of reversal methods are observed: 24-hr EDR, 12-hr EDR, 5-min flash reversal every 2 hours, and 3-min flash reversal every 2 hours. Membrane fouling occurred on a few occasions, however, chemical CIPs were able to remove the foulant and restore membrane performance. It likely that fouling was caused by organic matter, such as NOM in the diluate. As discussed in Section 2.2.1.3, organic fouling is common on the anion exchange membrane, which inhibits the passage of ions across the membranes. Other forms of fouling include scaling, colloidal, or biofouling. Fouling due to scaling is unlikely in this brine because calcium and magnesium are in very low concentrations due to the pretreatment of the drinking water source before it is treated with SIX® resins. Colloidal fouling is possible, however, the SEM images presented in the bench-scale study show much more carbon than silica compounds, which suggest there is more organic matter than colloids. Biofouling is also unlikely, even though there is a high biofouling potential (Section 4.4), because of the frequent CIPs and it is unlikely biofouling would be observed during about 600 hours of operation.

Based on the operational data, particularly current density and rate of concentrate conductivity increase, the best method of reversal is a 12-hr EDR. This EDR frequency preserved membrane performance in the F&B operation with both IEX brine types. However, a shorter EDR
may need to be investigated for the IEX Pilot Brine, due to the decreased performance at the end of the experiment. Additionally, flash reversals were observed to be insignificant in preserving performance of the membranes.

Preventative chemical CIPs were typically conducted at the end of each week (after approximately 96-hours of operation). After each CIP, a demineralization test was conducted to determine the effectiveness. The CIP every week was often enough to preserve membrane performance, however, further research should be conducted to determine if a CIP every 100 hrs is too often.

4.6. Discussion of Non-Selective Membrane Operation

Measuring the parameters of the EDNS operation address the forth objective of this thesis. The concentrate conductivity limit experiment shows an upper limit of conductivity at approximately 80 mS/cm to minimize the osmotic pressure across the membrane. However, more research needs to be conducted on the mass balance of the EDNS stage to determine ion passage from diluate into concentrate, as well as the amount of sulfate separation from NOM up until 80 mS/cm. These data also showed that water passage across the membranes is a disadvantage of these membranes, such that it inhibits concentrate conductivity beyond 80 mS/cm, therefore, limiting the concentration of sulfate in the final concentrate product. It can be concluded that there is a tradeoff with sulfate recovery – either high recovery of diluate with low purity sulfate concentrate (contamination due to NOM passage) or high sulfate recovery with low purity diluate product (better separation due to less osmotic pressure). In the case of PWN Technologies, the level of ED treatment depends on the market and what industry is willing to purchase the ED products. The NOM solution would be purchased by farmers to be used as a biostimulant in soils.
However, sulfates reduce the quality of the biostimulant and it would not be economical for the farmers to purchase a low-purity NOM solution. The sulfate solution would be sold to the glass or paper industry.

The pH adjustment experiment illustrates the challenges associated with separating sulfate from NOM; the more sulfate recovered, the more NOM passages through the membrane due to higher osmotic pressure. This experiment shows that performance of the stack decreased with decreasing the pH of the diluate. Therefore, lowering the diluate pH does not have any impact on sulfate recovery.

4.7. Discussion of Bench-Scale Test

The bench-scale experiments compared the impact of brine type, spacer size, and pretreatment of brine on spacer clogging over a 2-day period. These experiments address the third objective of this thesis: observe and measure the level of spacer clogging over time with respect to pressure increase and particle concentration in the influent and effluent.

During the experiments, significant pressure increase was experienced for all three brine types. The IEX Pilot and DNF Brines experienced the most pressure increase, whereas the Andijk III Brine shows the lowest over a 48-hour period. Additionally, pressure increase in the bench-scale unit was observed with IEX Pilot Brine comparing a standard spacer (450 µm) versus a larger spacer (750 µm). The standard spacer experienced a 0.25 bar increase compared to very slight pressure increase of 0.022 bar in the large spacer. The average particle load data confirmed that the standard spacer retained more particles of ≥15 µm in diameter. Finally, the pretreated brine experiments showed similar pressure behavior, such that pressure did not increase with pretreated IEX Pilot Brine with 10-micron filter, and only slightly increased with the 50-micron filtered brine
(0.073 bar). While the 50-micron filtered brine showed a greater increase in pressure, it is likely the 10-micron filter will clog much faster than the 50-micron filter. Therefore, a 50-micron filter is the most logical pretreatment method of these two.

4.8. Discussion of AOC and BPP Measurements on IEX Brine

The AOC and BPP experiments suggests biofouling might be an issue in electrodialysis due to the high concentrations of ATP on the SFS. These data show that AOC can be measured in desalinated brine (diluted or undiluted). However, AOC experiments should not be conducted on only one of the diluted or undiluted as there were varying conclusions: AOC of the undiluted brine suggests toxins are present inhibiting growth of NOX, but in the diluted sample, NOX inhibited the growth of P17. Therefore, these experiments should be done together, as they complement each for a well-rounded measurement of AOC.

BPP results showed high concentrations of ATP in IEX Pilot and DNF Brine, however, DNF brine was significantly higher. On full-scale operation of electrodialysis, DNF Brine will be the main feed source as the diluate, therefore, the high BPP results raise a concern for biofouling potential. As a result, Vaudevire et al 2016 suggest three hypotheses for the DNF Brine: acetate is not fully utilized which can promote growth after denitrification is complete; biomass in the denitrification process produce biopolymers and microbial products to sustain growth; and biomass may adapt to the high salt concentration during denitrification contact time.
CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

This chapter presents overall conclusions derived from the data collected on pilot operation and bench-scale particle fouling experiments. Recommendations for further research will also described in this section.

5.1. Mono-Selective Membrane, Pilot Operation Conclusions

Pilot operation was studied on two levels: batch and continuous F&B. Membrane performance during batch pilot operation was measured with the net change in conductivity and average current density of each 5-hr trial, speed of ion transfer, and percent change of ion concentration.

Batch experiments resulted in the following conclusions:

- RO rinsing partially cleaned the membranes after each 5-hr trial, these experiments cannot be used as an effective indicator to optimize reversal frequency; and

- Membrane performance is preserved with respect to ion passage (speed of transfer and percent change in ion concentrations) throughout the duration of both batch experiments due to high passage of monovalent ions with low passage of multivalent ions. However, preservation might also be attributed to RO rinsing after every 5-hr trial.
- Membrane performance during F&B pilot operation was measured by observing operational data (current density and conductivity), NOM and sulfate passage into the concentrate, ion selectivity over time, and physical and mechanical properties of the membranes over time. In addition to monitoring membrane and stack performance, preventative CIPs were conducted along with demineralization tests to compare CIP methods.

**F&B experiments resulted in the following conclusions:**

- Pilot operation with IEX Pilot Brine and Andijk III Brine shows overall stability with respect to current density and rate of concentrate conductivity increase;

- Quality of 90 mS/cm recovery stream (concentrate) stayed relatively constant with respect to NOM and sulfate passage. However, operation with IEX Andijk III Brine resulted in a higher quality solution (higher chloride to NOM/sulfate ratio) when compared to that of concentrate generated with IEX Pilot Brine as the diluate;

- 12-hr EDR showed the best results with respect to membrane performance using both IEX brines, however, further research should be conducted on more frequent EDRs (6-hr or 8-hr EDR) to prevent fouling;

- Membrane evaluation after 870 hours of operation concluded ion selectivity of the membranes did not decrease over time, and there are no physical or mechanical defects;

- Chemical CIPs were able to restore membrane performance after fouling;

- IEX Pilot Brine yielded a higher current density than the IEX Andijk III Brine, however NOM and sulfate concentrations are higher in the concentrate stream when using IEX Pilot
Brine as the diluate. This presents a trade-off: better stack performance or less NOM and sulfate contamination of the concentrate stream;

- Performance of the ED stack could be affected by type of electrolyte (sulfamic or sulfuric acid) or concentration of multivalent ions in the diluate;

- 0.1 N NaOH (less intensive) should be used for chemical CIP because membrane performance was comparable after each CIP method;

- Flash reversals were not an effective method for reversal; and

- Demineralization tests further concluded membrane performance does not significantly decrease over time.

5.2. Non-Selective Membrane, Pilot Operation Conclusions

Two experiments were conducted to observe how much the concentrate conductivity can increase, and if adjusting the pH of the raw diluate will improve separation of sulfate from NOM. Non-selective membranes were tested in batch operation to determine the maximum conductivity of the concentrate when using diluate pretreated with the mono-selective membranes.

Concentrate conductivity experiment resulted in the following conclusions:

- The upper limit of concentrate conductivity is approximately 65 mS/cm to minimize osmotic pressure across the membrane; and

- Confirms theory presented in (Lebon et al 2014), which identifies the trade-off of removing sulfates from the diluate, such that the more sulfate recovered, the more NOM passage across the membrane.
A challenge of the non-selective membrane operation is effectively separating sulfate from NOM. A possible remedy is to decrease the pH of the diluate to pH of the diluate from pH 9 to 5 however, this did not improve non-selective membrane performance.

**Adjusting diluate pH to improve separation of sulfate from NOM resulted in the following conclusions:**

- Adjusting the pH of the diluate did not improve sulfate separation from NOM; and
- Decrease in stack performance was observed when the pH was adjusted.

### 5.3. Bench-Scale Particle Fouling Unit Conclusions

The purpose of the bench-scale particle fouling unit experiments were to observe the effects of brine type, spacer size, and brine pretreatment on spacer fouling with respect to particles.

**The bench-scale experiments results in the following conclusions:**

- IEX Andijk III Brine shows the least amount of pressure increase over a 2-day experiment because the composition of the brine is lighter than the IEX Pilot and DNF with respect to rigid as well as amorphous particles.
- Large spacer (750 µm) spacer retains less particles, therefore less pressure increase; and
- Pretreatment with 50-micron filter results in comparable pressure increase to the 10-micron filter, therefore 50-micron filter should be used to reduce filter clogging potential.
- The SEM and EDX analysis suggests that the main constituents present on the spacers and AEM are organic matter, sodium chloride, and sodium sulfate. Silica components are also present which suggests there are diatoms present (Vermaas et al 2013), however the concentrations are low enough to not be significant.
- ATP accumulation on the spacer and membrane play a role in the pressure increase which lead to the BPP and AOC experiments to determine if biofouling would become an issue.

5.4. Recommendations for Further Research

- Further research to determine cause of fouling due to type of electrolyte or multivalent ion concentrations.
  - The F&B IEX Pilot Operation showed a significant decrease in membrane and stack performance towards the end of the experiment. This could be attributed to the change of electrolyte from sulfamic acid to sulfuric acid, OR from the increasing concentrations of NOM and sulfate over time. Fouling could be caused by one or both of these situations.
  - Experimentation of resin regeneration with recovered NaCl solution
    - The recovered sodium chloride solution (concentrate stream) will be used to regenerant IEX resins, therefore, used resins should be regenerated with the recovered solution to test its applicability.
    - In addition to sodium chloride recovery, bicarbonate is also separated from the diluate. The effect of bicarbonates in the regeneration process should be analyzed to determine if there is an accumulation of bicarbonate ions. A suggestion made by Erik Koreman, PWNT Senior Researcher, is to test the feasibility of switching from sodium chloride regeneration to bicarbonate regeneration solution. However, this may cause issues for the subsequent drinking water treatment processes if bicarbonate is not removed from the water.
  - Further testing on EDR frequency
Due to the challenge of having to manually reverse the pilot to run the EDR, the minimal reversal duration was an 8-hr/16-hr reversal, such that the system was reversed in the morning and evening each day.

If an automatic reversal was installed, shorter EDR times could be analyzed, such as a 5-hr, 8-hr, or 10-hr EDR.

- Continuous pilot run for longer duration between CIPs
  
  The pilot system was chemically cleaned almost every week (approximately every 4 days) while running the pilot with F&B operation because the system could not continuously run during the weekend due to the manual reversals.

  Continuous operation should be tested for longer periods in between CIPs to determine how often CIPs need to be conducted. Reducing the number of CIPs can reduce the costs of purchasing the chemicals as well as reduce the damage done on the membrane from over cleaning. Therefore, research should be conducted on the frequency of the CIP, such as testing the effects of conducting a CIP every two weeks, every month, or every other month. The data collected on current density and demineralization tests will then give a better idea of how frequent the CIP needs to be conducted.

- Spacer test improvements
  
  The bench-scale unit to observe particle fouling on spacers needs to be improved, such as reducing channeling through the SFS to avoid air bubbles at the outlet and adjusting the set-up to avoid the inlet hose bursting (i.e. use a different type hose with a higher psi rating).
- During the experiment, air bubbles formed at the end of the cell causing channeling of brine. The hoses used cannot withstand a high pressure and frequently burst, or required the pump speed to be decreased.

- Optimization of the denitrification process, with respect to the addition of acetate, to reduce biofouling potential in electrodialysis.

- If biofouling potential is high, even after acetate is reduced, which is likely, it might be interesting to test CIP methods mentioned in Table 2 to reduce biological attachment to the surface of the membranes.
REFERENCES


Vaudevire, E, Bonneau, J, Martijn, B, Cornelissen, E. Application of electrodialysis for by products recovery from saline brine to balance costs of zero discharge. 2015. IDAWC on Desalination and Water Reuse.

Vaudevire, E, Knezev, A, Prest, E. Biofouling potential IEX brine (Andijk 3 and pilot plant): Stage 1, Memorandum for PWN Technologies.


Zhang, Y, Pinoy, L, Meesschaert, B, Van der Bruggen, B. Separation of small organic ions from salts by ion-exchange membrane in electrodialysis. 2010. American Institute of Chemical Engineers. 57 (8).
APPENDIX A: ADDITIONAL EQUIPMENT FIGURES
Additional Pilot Study Descriptions

Figure 115 is an image of the EDR pilot system at PWNT. Figure 116 illustrates the location of pumps, valves, and pipes for the tanks in the pilot system. This set-up is consistent across all four diluate and concentrate tanks. The tank shown in Figure 116 stores diluate or concentrate to the NS stack. It has three return pipes (“C”, “D”, and “E”) because this pilot system has the ability to fill the tank directly leaving the MS ED stack, such that during the “bleeding cycle” the IEX brine will enter the NS stage tank instead of being wasted (Figure 13, Figure 16). The tanks for the MS stage only have 2 valves, one for concentrate return and one for IEX brine return. The electrolyte tank has only one return valve because the electrolyte does not come in contact with any other solution. This section will discuss the materials used for all three experiments.

Figure 115: EDR Pilot System at PWNT
Figure 116: Flows in and out of tank

(A) 275-L tank for dilute or concentrate; (B) pump and flow meter (IEX brine or concentrate from the tank to the rope filter); (C), (D), and (E) are retour pipes and valves into the tank returning from the ED tank; and (F) is where IEX brine or concentrate enters the tank from the external storage tanks.
Additional SFS Materials Description

The peristaltic pump was a Masterflex® L/S Variable-Speed Drive with 10-Turn Speed Control and Remote Capabilities from Cole-Parmer Instrument Company; Model Number 77521-47 (Figure 18). The peristaltic pump could operate with a flow of 0.36 mL/min – 3600 mL/min and drew the SIX® spent regenerant from the bottom of a 1000-L tank. The tank used a ALMO MMP71K4 propeller (1400 rpm) to continuously mix the IEX brine. An Endress+Hauser Cerabar T PMC131 pressure meter was used in conjunction with the Grant Squirrel SQ2010 Series data logger to gather pressure data for the duration of each experiment (Figure 19). The Cerabar T PMC 131 can measure pressure between 0 and 1 bar.
APPENDIX B: DETAILED METHODS FOR PILOT STUDY
Pilot Study

B.1 Mono-selective membrane batch study, Start-up and Operation

1. Drain concentrate and diluate tanks
2. Fill concentrate tank with 60 L of RO water
3. Fill diluate tank with 200 L of IEX brine from the pilot facility
4. Turn pilot system pumps on to measure the conductivity of each flow
5. Adjust the conductivity of the electrolyte to 20 mS/cm with sulfamic acid (or sulfuric acid if sulfamic acid is not available)
6. Adjust the conductivity of the concentrate to 75 mS/cm with saturated NaCl solution
7. Adjust the conductivity of the diluate to 45 mS/cm with saturated NaCl solution (increase conductivity) or RO water (decrease conductivity)
8. Take a 200 mL sample of concentrate and diluate for in-house laboratory measurements of initial concentrations of sulfate and NOM
9. Once every week take a 1-L sample to be sent to HWL to measure the initial concentration of sodium, chloride, bicarbonate, sulfate, total organic carbon, conductivity, and pH
10. Turn power on
   a. Voltage is set at 45 V
   b. Amperage is set at maximum of 60 A to allow current to vary throughout the experiment
11. Run pilot system for 5 hours
12. Turn off power and take a 200 mL sample of concentrate and diluate for in-house laboratory measurements of final concentrations of sulfate and NOM
13. Once every week take a 1-L sample to be sent to HWL to measure the final concentration of sodium, chloride, bicarbonate, sulfate, total organic carbon, conductivity, and pH

14. Transfer treated IEX brine into the diluate tank of the non-selective stage

15. Drain the concentrate tank

16. Rinse concentrate and diluate tanks with RO water

17. Fill tanks with RO water and rinse the pipes and ED stack in the pilot by turning on the pilot system pumps and flushing RO water through the stack

18. Let clean water recirculate through the stack for at least 15 minutes to insure most organics are flushed out of the system

**B.2 Mono-selective membrane batch study, EDR**

1. Drain concentrate and diluate tanks

2. Fill the diluate tank with 60 L of RO water (reversing flow paths, so concentrate flow path is now the diluate flow path)

3. Fill concentrate tank with 200 L of IEX brine from the pilot facility (reversing flow paths, so diluate flow path is now the concentrate flow path)

4. Swap the anode and cathode connections (anode now inserted into the cathode port and cathode now insert into the anode port)


**B.3 Mono-selective Continuous Feed and Bleed Testing, Start-up and Operation**

1. Drain concentrate and diluate tanks

2. Fill concentrate tank with 200 L of RO water

3. Fill diluate tank with 200 L of IEX brine from pilot facility or Andijk III treatment facility
4. Fill external volume storage for concentrate with RO water and connect tank to pilot system

5. Fill external volume storage for diluate with IEX brine either from the pilot facility or Andijk III treatment facility and connect tank to pilot system

6. Turn pilot system pumps on to measure the conductivity of each flow

7. Adjust the conductivity of the electrolyte to 20 mS/cm with sulfamic acid (or sulfuric acid if sulfamic acid is not available)

8. Adjust the conductivity of the concentrate to 75 mS/cm with saturated NaCl solution

9. Do not adjust diluate conductivity

10. Take a 200 mL sample of concentrate and diluate for in-house laboratory measurements of initial concentrations of sulfate and NOM

11. Once every week take a 1-L sample to be sent to HWL to measure the initial concentration of sodium, chloride, bicarbonate, sulfate, total organic carbon, conductivity, and pH

12. Change the pilot system settings to run in continuous feed and bleed
   a. Set concentrate to bleed at 90 mS/cm
   b. Set diluate to bleed at 19 mS/cm if IEX brine is from pilot facility
   c. Set diluate to bleed at 14 mS/cm if IEX brine is from Andijk III facility
   d. Set pilot to automatically refill after bleeding
   e. Set pilot to deposit bled diluate into Stage 2, only if planning to the non-selective membranes the following day

13. Turn power on
   a. Voltage is set at 45 V
b. Amperage is set at maximum of 60 A to allow current to vary throughout the experiment

14. Allow system to run continuously over night for four days

15. Refill external tanks as needed

16. Adjust the electrolyte conductivity at the beginning and end of each day

17. During the bleeding of the system, take a 200 mL sample of concentrate and diluate directly coming from the ED stack for in-house laboratory measurements of final concentrations of sulfate and NOM

18. Once every week take a 1-L sample to be sent to HWL to measure the final concentration of sodium, chloride, bicarbonate, sulfate, total organic carbon, conductivity, and pH

19. Drain and rinse the diluate and concentrate tanks with RO water

20. Fill tanks with RO water and rinse the pipes and ED stack in the pilot by turning on the pilot system pumps and flushing RO water through the stack

21. Conduct a CIP at the end of the week

**B.4 Mono-selective Continuous Feed and Bleed Testing, EDR**

1. Concentrate and diluate tanks are NOT drained in this EDR

2. Turn off the pilot system by first shutting off the electricity in the ED stack and then turn power off in the pilot system

3. Disconnect the diluate and concentrate inlet hoses that are connected to the ED stack

4. Connect the concentrate hose to the diluate inlet and the diluate hose to the concentrate inlet

5. Disconnect the diluate and concentrate outlet hoses that are connected to the ED stack
6. Connect the concentrate hose to the diluate outlet and the diluate hose to the concentrate outlet

7. Disconnect the anode and cathode from the stack and place the anode in the cathode port and cathode in the anode port.

8. Turn the pilot system back on and insure the continuous feed and bleed settings are correct


B.5 Non-selective membrane batch study

1. Drain concentrate and diluate tanks

2. Fill concentrate tank with 60 L of RO water

3. Fill diluate tank with 200 L of IEX brine from the pilot facility

4. Turn pilot system pumps on to measure the conductivity of each flow

5. Adjust the conductivity of the electrolyte to 20 mS/cm with sulfamic acid (or sulfuric acid if sulfamic acid is not available)

6. Adjust the conductivity of the concentrate to 10 mS/cm with saturated Na$_2$SO$_4$ solution
   a. After the first trial of NS stage, no adjustment to concentrate is needed because the goal is to track how high the conductivity of the concentrate can increase to

7. Take a 200 mL sample of concentrate and diluate for in-house laboratory measurements of initial concentrations of sulfate and NOM

8. Turn power on
   a. Voltage is set at 45 V
   b. Amperage is set at maximum of 60 A to allow current to vary throughout the experiment
9. Run pilot system for 5 hours

10. Turn off power and take a 200 mL sample of concentrate and diluate for in-house laboratory measurements of final concentrations of sulfate and NOM

11. Drain the diluate tank

12. Do NOT drain the concentrate tank

13. Rinse diluate tanks with RO water

14. Fill tanks with RO water and rinse the pipes and ED stack in the pilot by turning on the pilot system pumps and flushing RO water through the stack

15. Let clean water recirculate through the stack for at least 15 minutes to insure most organics are flushed out of the system

**B.6 Cleaning in place (CIP)**

B.6.1 METHOD ONE, 0.1 N HCL AND 0.1 N NAOH

1. Flow through the ED stack was reversed
   a. Diluate inlet to diluate outlet, diluate outlet to diluate inlet
   b. Concentrate inlet to concentrate outlet, concentrate outlet to concentrate inlet

2. RO water only flushed through the stack for approximately 30 minutes
   a. Concentrate and diluate tanks were drained

3. 0.1 N HCl solution run through the stack for 20 minutes

4. 2 L of HCl, 10%

5. 60 L RO water

6. Concentrate and diluate tanks were drained after 20 minutes

7. RO water flushed through the stack for ~15-20 minutes
8. Make sure conductivity of both concentrate/diluate are below 5 mS/cm

9. Concentrate and diluate tanks were drained

10. 0.1 N NaOH solution run through the stack for 40 minutes
    a. 600 mL of NaOH, 32%
    b. 60 L RO water
    c. Concentrate and diluate tanks were drained after 40 minutes
    d. RO water flushed through the stack for 20 minutes
    e. Concentrate and diluate tanks were drained

11. 0.1 N HCl solution run through the stack for 20 minutes

12. 2 L of 10% HCl

13. 60 L RO water

14. Concentrate and diluate tanks were drained after 20 minutes

15. RO water flushed through the stack for 20 minutes

B.6.2 METHOD TWO, 0.1 N HCL, 2.5% NAOH

1. Flow through the ED stack was reversed
   a. Diluate inlet to diluate outlet, diluate outlet to diluate inlet
   b. Concentrate inlet to concentrate outlet, concentrate outlet to concentrate inlet

2. RO water only flushed through the stack for approximately 20 minutes
   a. Concentrate and diluate tanks were drained

3. 0.1 N HCl solution run through the stack for 10 minutes
   a. 2 L of HCl, 10%
   b. 60 L RO water
c. Concentrate and diluate tanks were drained after 10 minutes
d. RO water flushed through the stack for 10 minutes
e. Concentrate and diluate tanks were drained

4. 2.5% NaOH solution run through the stack for 30 minutes
   a. 1 L of saturated NaCl solution was added to 60 L of RO water
   b. NaCl flushed for 5 minutes
c. 4.6 L of NaOH was added to the NaCl solution
d. NaOH CIP ran for 30 minutes
e. Concentrate and diluate tanks were drained
   b. RO water flushed through the stack for 10 minutes
c. Concentrate and diluate tanks were drained

5. 0.1 N HCl solution run through the stack for 10 minutes
   a. 2 L of 10% HCl
   b. 60 L RO water
c. Concentrate and diluate tanks were drained after 10 minutes
d. RO water flushed through the stack a few times

B.6.3 Demineralization Test

1. Drain concentrate and diluate tanks

2. Fill both concentrate and diluate tanks with 100 L of 30 mS/cm NaCl solution (RO water and saturated NaCl solution)

3. Adjust the electrolyte conductivity to 20 mS/cm with sulfamic acid (or sulfuric acid if sulfamic in unavailable) to increase conductivity, or RO water to decrease conductivity
4. Turn pilot system and pumps on to insure the conductivity of all three flow streams are correct

5. Check pilot settings to insure it will run in batch, not feed and bleed

6. Adjust the pilot setting to keep current constant, but vary voltage
   a. Voltage is set to maximum, 100 V
   b. Current is set at 6 A

7. Take a 100-mL sample of concentrate and diluate before turning the electricity on in the ED stack

8. Measure pH and temperature

9. Turn electricity on in the ED stack

10. Take one sample every 5 minutes to measure pH and temperature in both the concentrate and diluate

11. Turn electricity and power off in the pilot system after 7 samples have been measures (30-minutes of running pilot)

   **Bench-scale Study**

1. Identify which experimental trial will be conducted from the list below
   a. Validation test with standard-sized particles (Duke Standards, NIST Traceable Polymer, $1.5 \times 10^8$ particles with a diameter of $5.021 \mu m \pm 0.041 \mu m$,) and standard spacer, 450 µm
   b. Pilot IEX brine and standard spacer, 450 µm
   c. Pilot IEX brine and big spacer, 750 µm
   d. Pilot IEX brine filtered with 1-micron filter and standard spacer, 450 µm
e. Pilot IEX brine filtered with 5-micron filter and standard spacer, 450 µm
f. Andijk III brine and standard spacer, 450 µm

2. Fill the 1000-L tank with IEX brine (from pilot facility or Andijk III facility)
   a. If conducting experiment “a”, fill a gallon bucket with RO water and standard particles. Place bucket on stir plate with a stir bar

3. Place the ALMO MMP71K4 propeller in the tank and turn on to keep particles in the IEX brine suspended

4. Cut the appropriate spacer and anion exchange membrane to the dimensions 4 cm x 20 cm for the experiment chosen in Step 1

5. Remove the top cover of the FS unit and the top silicone sheet (Figure 21)

6. Place the anion exchange membrane on the bottom silicone sheet and the spacer on top of the membrane

7. Place the top silicone sheet directly over the membrane/spacer pair such that the spacer will be flush up against the transparent cover of the unit (Figure 21)

8. Place the transparent cover on top of the silicone sheet and tighten the fourteen bolts

9. If the brine is pre-treated (experiments “d” or “e” above), attached the appropriately sized filter between the tank and peristaltic pump

10. Connect the hose of the cell unit to the 1000-L tank, which passes through the peristaltic pump (Figure 118)
Figure 118: KWR Spacer unit schematic, no brine pre-treatment

a. If brine is pre-treated, the hose will be connected to the tank, then the filter, then pass through the pump and finally the inlet of the unit (Figure 119)

Figure 119: KWR Spacer unit schematic, brine pre-treatment

11. Turn pump on and allow the system to run for 48 hours
12. Before shutting off the pump, collect 1-L influent and 1-L effluent in clean bottles
13. Send samples to KWR to be analyzed for particle counting
14. After the experiment is completed, turn pump off and remove the transparent cell from the pressure meter
15. Remove the bolts and the top of cell
16. Using sterile equipment supplied by HWL, cut a 10 cm² piece of spacer and membrane and place into sample vials filled with 10 mL of ATP-free water
17. Place the remaining spacer and membrane pair in a sterile petri dish to dry
18. Set aside and covered until SEM/EDX analysis at Wetsus
APPENDIX C: In-House HACH Methods
Sulfate

Turbidimetric Method
LR (40 to 150 mg/L SO$_4^{2-}$)

Method 10227
TNTplus™ 864

Scope and Application: For drinking water, wastewater, raw water and process control

Test preparation

How to use instrument-specific information

The Instrument-specific information table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 392 Instrument-specific information

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Light shield</th>
</tr>
</thead>
<tbody>
<tr>
<td>DR 6000</td>
<td>—</td>
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<tr>
<td>DR 5000</td>
<td>—</td>
</tr>
<tr>
<td>DR 3900</td>
<td>LZV849</td>
</tr>
<tr>
<td>DR 3800, DR 2800</td>
<td>LZV646</td>
</tr>
</tbody>
</table>

Before starting the test:

Install the light shield if applicable (see Instrument-specific information).

Please read Safety Advice and Expiration Date on package.

Refer to Accuracy check to verify results.

Recommended sample, sample vial and reagent temperature is 15–25 °C (59–77 °F). Recommended reagent storage temperature is 15–25 °C (59–77 °F).

Recommended sample pH is 3–10.

TNTplus methods are activated from the Main Menu screen when the sample vial is inserted into the sample cell holder.

Collect the following items:

<table>
<thead>
<tr>
<th>Item</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate LR TNTplus 864 Reagent Set</td>
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</tr>
<tr>
<td>Light Shield (see Instrument-specific information)</td>
<td>1</td>
</tr>
<tr>
<td>Pipettor, variable, 1–5 mL</td>
<td>1</td>
</tr>
<tr>
<td>Pipettor Tips for 1–5 mL Pipettor</td>
<td>1</td>
</tr>
</tbody>
</table>

See Consumables and replacement items for reorder information.
Sulfate

**Sulfate, LR, TNTplus864**

1. Carefully pipet 5.0 mL of sample into the TNT884 vial.
2. Add one level spoonful of Reagent A to vial.
3. Immediately cap the vial and invert for 2 minutes.
4. Wipe the outside of the vial to remove fingerprints and other marks.
5. Insert the vial into the cell holder.

The instrument reads the barcode, then selects and performs the correct test. Results are in mg/L $\text{SO}_4^{2-}$.

No instrument Zero is required.

**Sample collection, preservation and storage**

- Analyze samples within 3 hours after collection for best results.
- Samples may be stored up to 28 days at 4 °C (39 °F).
- Warm samples to room temperature before analysis.

**Accuracy check**

*Standard solution method with sulfate standard*

*Note: Refer to the instrument user manual for specific software navigation instructions.*

Required for accuracy check:

- Sulfate standard solution, 50 mg/L or 100 mg/L

1. Use 5.0 mL of the prepared standard in place of the sample.
2. Follow the *Sulfate, LR, TNTplus864* test.
Sulfate

Standard solution method with mixed parameter standard
Use a mixed-parameter standard, which contains sulfate and other common ions that may be present in samples of a given type. The Drinking Water Inorganics Standard and the Wastewater Effluent Standard both contain 50 mg/L SO₄, as well as other ions.

Required for accuracy check:
- Wastewater Effluent Standard or Drinking Water Inorganics Standard
1. Use 5.0 mL of the mixed parameter standard in place of the sample.
2. Follow the Sulfate, LR, TNTplus864 test.

Summary of method
Sulfate ions in the sample react with barium chloride in aqueous solution and form a precipitate of barium sulfate. The resulting turbidity is measured photometrically at 430 nm.

Consumables and replacement items

<table>
<thead>
<tr>
<th>Required reagents</th>
<th>Description</th>
<th>Quantity/Test</th>
<th>Unit</th>
<th>Catalog number</th>
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</thead>
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<td>TNT864</td>
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<table>
<thead>
<tr>
<th>Required apparatus</th>
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<th>Quantity/Test</th>
<th>Unit</th>
<th>Catalog number</th>
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</thead>
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<td>Pipettor, variable volume, 1.0–5.0 mL</td>
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<td>each</td>
<td>BBP065</td>
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</tr>
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<td>Pipettor Tips, for BBP065 pipettor</td>
<td>1</td>
<td>75/pkg</td>
<td>BBP068</td>
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<table>
<thead>
<tr>
<th>Recommended standards and apparatus</th>
<th>Description</th>
<th>Unit</th>
<th>Catalog number</th>
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<td>Mixed Parameter, Drinking Water Inorganics Standard</td>
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<tr>
<td>Mixed Parameter, Wastewater Effluent Standard</td>
<td>500 mL</td>
<td>2833249</td>
<td></td>
</tr>
<tr>
<td>Sulfate Standard Solution, 60 mg/L SO₄</td>
<td>500 mL</td>
<td>257849</td>
<td></td>
</tr>
<tr>
<td>Sulfate Standard Solution, 100 mg/L SO₄</td>
<td>500 mL</td>
<td>89149</td>
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<tr>
<td>Water, deionized</td>
<td>4 L</td>
<td>27256</td>
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<table>
<thead>
<tr>
<th>Optional reagents and apparatus</th>
<th>Description</th>
<th>Unit</th>
<th>Catalog number</th>
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</thead>
<tbody>
<tr>
<td>Bottle, 500-mL sampling, low-density polyethylene, with cap</td>
<td>12/pkg</td>
<td>2087079</td>
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<tr>
<td>Test Tube Rack, 13-mm vials</td>
<td>each</td>
<td>2497900</td>
<td></td>
</tr>
<tr>
<td>Wipers, disposable</td>
<td>280/pkg</td>
<td>2097000</td>
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</tr>
</tbody>
</table>
Organic Carbon, Total

Direct Method
1.5 to 30.0 mg/L C (LR)

Method 10267
TNTplus 810

Scope and application: For wastewater, drinking water, surface water and process water analyses.

Test preparation

Before starting

DR 3900, DR 3800, DR 2800: Install the light shield in Cell Compartment #2 before this test is started. Review the safety information and the expiration date on the package.

Use the DRB reactor with 13-mm wells for the digestion. If the reactor has 16-mm wells, insert adapter sleeves into the wells. Make sure to digest the samples at 100 °C. Higher temperatures may cause the vials to break apart.

Be careful with the vials after the digestion. Pressure increases in the vials during the digestion and can cause the vials to break apart.

Use only the TOC-X5 shaker to remove total inorganic carbon (TIC) from the sample. Carbon dioxide from the air can contaminate the sample. Do not open the indicator vial before the shaker operation is complete. Immediately install the double cap on the indicator vial after the cap is removed, then immediately install the other side of the double cap on the sample vial.

The formation of crystals in the sample vial does not affect the result.

The recommended temperature for reagent storage is 2–8 °C (35–46 °F).

The recommended sample pH is 3–10.

If the sample contains particles, dilute the sample. Use the diluted sample in the test procedure. Multiply the test result by the dilution factor.

After both vials are attached to the double cap, keep the vial assembly together. Put the vial assembly in the plastic packaging after the analysis.

DR 1900: Go to All Programs>LCK or TNTplus Methods>Options to select the TNTplus number for the test. Other instruments automatically select the method from the barcode on the vial.

Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.

Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

<table>
<thead>
<tr>
<th>Description</th>
<th>Quantity</th>
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</thead>
<tbody>
<tr>
<td>Total Organic Carbon, LR TNTplus 810 Reagent Set</td>
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</tr>
<tr>
<td>DRB200 reactor with 13-mm wells</td>
<td>1</td>
</tr>
<tr>
<td>TOC-X5 shaker</td>
<td>1</td>
</tr>
<tr>
<td>Pipet, adjustable volume, 1.0–5.0 mL</td>
<td>1</td>
</tr>
<tr>
<td>Pipet tips, for 1.0–5.0 mL pipet</td>
<td>1</td>
</tr>
<tr>
<td>Test tube rack</td>
<td>1</td>
</tr>
</tbody>
</table>

Refer to Consumables and replacement items on page 4 for order information.
Sample collection

- Collect samples in clean glass bottles.
- Homogenize samples that contain solids to get a representative sample.
- Rinse the sample bottle several times with the sample to be collected.
- Fill the bottle completely full, then tighten the cap on the bottle.
- Analyze the samples as soon as possible for best results.
- Acid preservation is not recommended.

Test procedure

1. Remove the cap from a clear vial. Use a pipet to add 2 mL of sample to the vial.
2. Insert the uncapped sample vial into the TOC-X5 shaker. Make sure that the vial is pushed all the way down into the shaker. Move the fan over the vial.
3. Push the on/off switch to start the shaker. Operate the shaker for 5 minutes.
4. When the shake time is complete, remove the cap from a blue indicator vial. Immediately install and tighten a double cap on the indicator vial with the barcode label toward the vial.
5. Immediately invert the indicator vial, then install and tighten the other side of the double cap on the sample vial. Hold the vial assembly vertically.
6. Insert the vial assembly into the DRB reactor (indicator vial on top).
7. Increase the vial assembly temperature for 2 hours at 100 °C.
8. Let the vial assembly cool completely to room temperature. Make sure that the vials cool completely. Warm vials will give high results.
Interferences

The table that follows shows the substances that were tested for interference and did not interfere up to the levels shown.

<table>
<thead>
<tr>
<th>Interfering substance</th>
<th>Interference level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium</td>
<td>200 mg/L</td>
</tr>
<tr>
<td>Calcium</td>
<td>2000 mg/L as CaCO₃</td>
</tr>
<tr>
<td>Chloride</td>
<td>1000 mg/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>2000 mg/L as CaCO₃</td>
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<tr>
<td>TIC</td>
<td>250 mg/L</td>
</tr>
</tbody>
</table>

Accuracy check

Standard solution method

Use the standard solution method to validate the test procedure, the reagents and the instrument.

Items to collect:
- 1000-mg/L C TOC Standard Solution
- 500-mL volumetric flask, Class A
- 200-mL volumetric flask, Class A
- 50-mL volumetric pipet, Class A and pipet filler safety bulb
- 20-mL volumetric pipet, Class A and pipet filler safety bulb
- Organic-free water

1. Prepare a 100-mg/L C stock solution as follows:
   a. Use a pipet to add 20 mL of a 1000-mg/L C standard solution into a 200-mL volumetric flask.
   b. Dilute to the mark with organic-free water. Mix well.

2. Prepare a 10-mg/L C standard solution as follows:
   a. Use a pipet to add 50 mL of a 100-mg/L C stock solution into a 500-mL volumetric flask.
   b. Dilute to the mark with organic-free water. Mix well. Prepare this solution daily.

3. Use the test procedure to measure the concentration of the prepared standard solution.

4. Compare the expected result to the actual result.

Note: The factory calibration can be adjusted slightly with the standard adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then
used for all test results. This adjustment can increase the test accuracy when there are slight variations in the reagents or instruments.

Method performance
The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

<table>
<thead>
<tr>
<th>Program</th>
<th>Standard</th>
<th>Precision (95% confidence interval)</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNTplus 810</td>
<td>10 mg/L C</td>
<td>9.72–10.28 mg/L C</td>
<td>0.4 mg/L C</td>
</tr>
</tbody>
</table>

Summary of method
The total inorganic carbon (TIC) in the sample is first removed during the shaker operation. The sample is then digested to oxidize the total organic carbon (TOC) in the sample to carbon dioxide (CO₂). The CO₂ from the digested sample goes through the membrane in the double cap to the indicator vial and causes the indicator solution to change color. The color of the indicator solution is measured by the spectrophotometer. The measurement wavelength is 435 nm.

Consumables and replacement items

<table>
<thead>
<tr>
<th>Description</th>
<th>Quantity/test</th>
<th>Unit</th>
<th>Item no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Organic Carbon Reagent Set, LR, TNTplus</td>
<td>1</td>
<td>25/pkg</td>
<td>TNT810</td>
</tr>
</tbody>
</table>

Required apparatus

<table>
<thead>
<tr>
<th>Description</th>
<th>Quantity/test</th>
<th>Unit</th>
<th>Item no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DRB 200 Reactor, 115 VAC option, 9 x 13 mm + 2 x 20 mm, 1 block</td>
<td>1</td>
<td>each</td>
<td>DRB20001</td>
</tr>
<tr>
<td>DRB 200 Reactor, 230 VAC option, 9 x 13 mm + 2 x 20 mm, 1 block</td>
<td>1</td>
<td>each</td>
<td>DRB20005</td>
</tr>
<tr>
<td>Pipet, adjustable volume, 1.0–5.0 mL</td>
<td>1</td>
<td>each</td>
<td>BPB068</td>
</tr>
<tr>
<td>Pipet tips, for 1.0–5.0 mL pipet</td>
<td>1</td>
<td>75/pkg</td>
<td>BPB068</td>
</tr>
<tr>
<td>Test tube rack</td>
<td>1</td>
<td>each</td>
<td>1864100</td>
</tr>
<tr>
<td>TOC-X5 shaker</td>
<td>1</td>
<td>each</td>
<td>LOV148.99.00002</td>
</tr>
<tr>
<td>Wipes, disposable</td>
<td>1</td>
<td>280/pkg</td>
<td>2097000</td>
</tr>
</tbody>
</table>

Recommended standards

<table>
<thead>
<tr>
<th>Description</th>
<th>Unit</th>
<th>Item no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC Standard Solution Ampule (KHP Standard, 1000-mg/L C)</td>
<td>5/pkg</td>
<td>2791505</td>
</tr>
</tbody>
</table>

Optional reagents and apparatus

<table>
<thead>
<tr>
<th>Description</th>
<th>Unit</th>
<th>Item no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor adapter sleeves, 16 mm to 13 mm diameter, for TNTplus vials</td>
<td>5/pkg</td>
<td>2895805</td>
</tr>
<tr>
<td>Ampule Breaker, 2-mL PourRite® Ampules</td>
<td>each</td>
<td>2484600</td>
</tr>
<tr>
<td>Flask, volumetric, Class A, 500-mL glass</td>
<td>each</td>
<td>1457449</td>
</tr>
<tr>
<td>Flask, volumetric, Class A, 200-mL</td>
<td>each</td>
<td>1457445</td>
</tr>
<tr>
<td>Pipet, volumetric, Class A, 50-mL</td>
<td>each</td>
<td>1451541</td>
</tr>
<tr>
<td>Pipet, volumetric Class A, 20-mL</td>
<td>each</td>
<td>1451520</td>
</tr>
<tr>
<td>Pipet filler, safety bulb</td>
<td>each</td>
<td>1465100</td>
</tr>
<tr>
<td>Description</td>
<td>Unit</td>
<td>Item no.</td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>-------</td>
<td>----------</td>
</tr>
<tr>
<td>Potassium Acid Phthalate (KHP), ACS</td>
<td>500 g</td>
<td>31534</td>
</tr>
<tr>
<td>Water, organic-free</td>
<td>500 mL</td>
<td>2641549</td>
</tr>
</tbody>
</table>
APPENDIX D: PRIOR PWNT RESEARCH ON ED, SUPPORTING INFORMATION
D.1 Additional Information: Bench-Scale Study on Ion Separation of IEX Brine

Table 17 outlines the parameters of the mono- and non-selective membranes used in this study. The two types of membranes were tested separately, such that mono- and non-selective membranes were never used in the PCCell ED 64002 cell unit at the same time.

<table>
<thead>
<tr>
<th>Name</th>
<th>Information</th>
<th>Active surface area (cm²)</th>
<th>Surface potential (Ω.cm²)</th>
<th>Thickness (µm)</th>
<th>Chemical stability (pH)</th>
<th>Functional groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCMVK</td>
<td>Mono-selective cation e.m</td>
<td>64</td>
<td>-</td>
<td>100</td>
<td>0-9</td>
<td>Sulfonic Acid</td>
</tr>
<tr>
<td>PCMVA</td>
<td>Mono-selective anion e.m</td>
<td>64</td>
<td>20</td>
<td>110</td>
<td>-</td>
<td>Ammonium</td>
</tr>
<tr>
<td>PCSK</td>
<td>Non-selective cation e.m</td>
<td>64</td>
<td>2,5</td>
<td>160-200</td>
<td>0-11</td>
<td>Sulfonic Acid</td>
</tr>
<tr>
<td>PC Acid 100 PEEK</td>
<td>Non-selective anion e.m</td>
<td>64</td>
<td>-</td>
<td>80</td>
<td>0-10</td>
<td>Ammonium</td>
</tr>
</tbody>
</table>

Table 18 and Table 3 outline the conditions of each stream including the flow rate, volume, and chemical composition. The mono-selective experiments with the PCCell ED 64002 cell unit was operated at different current densities (56, 103, and 164 A/m²) while the voltage was varied until it reached the maximum voltage of 20 V. The cell unit was run until the conductivity was below 0.7 mS/cm for the synthetic brine and 17-18 mS/cm (80-90% Cl⁻ transfer) for the PWNT IEX brine. The diluate which was treated with the mono-selective membranes was saved and then treated with the non-selective membranes. The non-selective experiments with the PCCell ED 64002 cell unit was operated at different current densities (41, 56, and 103 A/m²) while the voltage was varied until it reached the maximum voltage of 20 V.
### Table 18: Experimental setup (Bonneau et al 2014)

<table>
<thead>
<tr>
<th>Stream</th>
<th>Flow rate (L/h)</th>
<th>Volume (L)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diluate</td>
<td>60</td>
<td>1.5</td>
<td>Synthetic brine</td>
</tr>
<tr>
<td>Concentrate</td>
<td>60</td>
<td>1.5</td>
<td>NaCl solution (0,5%)</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>160</td>
<td>5</td>
<td>NaCl solution (2,93%)</td>
</tr>
</tbody>
</table>

*Information is borrowed from Dutch reports indicating that the convention in this report is different than in the US so (,) is used instead of (.)

### Table 19: Diluate characteristics (Bonneau et al 2014)

<table>
<thead>
<tr>
<th>Brine</th>
<th>[Cl(^{-})] (g/L)</th>
<th>[SO(_{4})(^{2-})] (g/L)</th>
<th>[HCO(_{3})(^{-})] (g/L)</th>
<th>[Na(^{+})] (g/L)</th>
<th>pH</th>
<th>Conductivity at 23°C (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic</td>
<td>9.0</td>
<td>8.0</td>
<td>3.8</td>
<td>11.1</td>
<td>8</td>
<td>35.1</td>
</tr>
<tr>
<td>PWNT IEX</td>
<td>6.7</td>
<td>7.9</td>
<td>4.1</td>
<td>--</td>
<td>7.2</td>
<td>31.3</td>
</tr>
</tbody>
</table>

D.1.1 Study Results and Discussion

The PCMVK/PCMVA mono-selective membranes were first analyzed with synthetic brine at 56 A/m\(^2\) to assess ion passage across the membranes. Figure 120 illustrates the concentration of chloride, bicarbonate, and sulfate during the 7-hour experiment. Chloride concentration was transferred first between t=0 and t=5 hours. Bicarbonate was transferred next, beginning when chloride concentration was approximately 20% remaining, around t=3.5 hours. All bicarbonates were transferred by t=5.5 hours. Sulfate begins to transfer around t=4.5 hours when only 20% of the total concentration of monovalent ions remain in the diluate. The order at which the ions are transferred depend on steric-hindrance effect, size of ion, and electric-repulsion.
PWNT IEX brine was also treated with PCMVK/PCMVA mono-selective membranes at 56 A/m² to assess ion passage across the membranes. Figure 12 illustrates the concentration of chloride, bicarbonate, and sulfate during the 3.5-hour experiment. Chloride concentration was transferred first between t=0 and t=2.5 hours. Bicarbonate was transferred next, beginning when chloride concentration was approximately 20% remaining, around t=2 hours. All bicarbonates were transferred by t=3.25 hours. Sulfate is retained in the diluate during the entire experiment. Bonneau et al. 2014 suggests that the presence of NOM in the diluate assisted in better separation of chloride from sulfate.

In addition to treating the synthetic brine and PWNT IEX brine at 56 A/m², current densities of 103 and 164 A/m² were also tested for each brine type. The purpose of testing all three current densities is to determine the optimum current density with respect to ion separation (selectivity to monovalent ions while using the mono-selective membranes). Table 20 and Table 21 compare the ion selectivity for Cl⁻ and HCO₃⁻ at different current densities for synthetic and PWNT IEX brine, respectively. The ion selectivity of chloride and bicarbonate in the PWNT IEX
brine is higher than that of the synthetic brine. As previously stated, Bonneau et al 2014 suggests that the NOM presence in the PWNT IEX brine promotes better separation of the ions. It can also be concluded from this data that 103 A/m² is the most efficient current density setting to achieved the highest ion selectivity in every case (both synthetic and PWNT IEX brine).

**Table 20: Impact of current density for synthetic brine separation with the mono-selective stack (Bonneau et al 2014)**

<table>
<thead>
<tr>
<th>Current density (A/m²)</th>
<th>Experiment duration (min)</th>
<th>Selectivity Cl/SO₄²⁻</th>
<th>Selectivity Cl/HCO₃⁻</th>
<th>Selectivity HCO₃⁻/SO₄²⁻</th>
<th>Slope Cl⁻ (Mass transfer in g/day)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>56</td>
<td>195</td>
<td>0.832</td>
<td>0.466</td>
<td>0.598</td>
<td>-80.6</td>
<td>0.9992</td>
</tr>
<tr>
<td>103</td>
<td>105</td>
<td>0.904</td>
<td>0.467</td>
<td>0.756</td>
<td>-147.4</td>
<td>0.9998</td>
</tr>
<tr>
<td>164</td>
<td>71</td>
<td>0.789</td>
<td>0.388</td>
<td>0.578</td>
<td>-217.6</td>
<td>0.9911</td>
</tr>
</tbody>
</table>

*Information is borrowed from Dutch reports indicating that the convention in this report is different than in the US so (,) is used instead of (.)

**Table 21: Impact of current density for PWNT IEX brine separation with the mono-selective stack (Bonneau et al 2014)**

<table>
<thead>
<tr>
<th>Current density (A/m²)</th>
<th>Selectivity Cl/SO₄²⁻</th>
<th>Selectivity Cl/HCO₃⁻</th>
<th>Selectivity HCO₃⁻/SO₄²⁻</th>
<th>Slope Cl⁻ (Mass transfer in g/day)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>56</td>
<td>0.991</td>
<td>0.645</td>
<td>0.954</td>
<td>-83.8</td>
<td>0.9996</td>
</tr>
<tr>
<td>103</td>
<td>0.998</td>
<td>0.760</td>
<td>0.986</td>
<td>-159.8</td>
<td>0.9998</td>
</tr>
<tr>
<td>164</td>
<td>0.990</td>
<td>0.621</td>
<td>0.957</td>
<td>-231.1</td>
<td>0.9986</td>
</tr>
</tbody>
</table>

*Information is borrowed from Dutch reports indicating that the convention in this report is different than in the US so (,) is used instead of (.)

This study also analyzed the impact of current density on non-selective membranes for brine that has been pre-treated with the mono-selective membranes. Figure 121 and Figure 122 show the diluate concentrations and power applied to the stack with 41 A/m². All chloride and bicarbonate ions were transferred between t=0 and t=3.5 hours. Sulfate concentration steadily decreases to approximately 1 mg/L (90% passage) over the 3.5-hour experiment. The current density was set at a constant 41 A/m² and the voltage was varied. Lower voltage indicates that a lower amount of energy is required for ion passage, whereas a high voltage indicates that a lot of
power is required to pass ions across the membrane. Therefore, Figure 122 indicates once chloride and bicarbonate ions are depleted, it takes more energy to transfer sulfate ions.

Figure 121: Diluate concentrations with IEX brine, non-selective stack and \(i=41\) \(A/m^2\) (Bonneau et al 2014)

Figure 122: Voltage and intensity applied, IEX brine, non-selective stack and \(i=41\) \(A/m^2\) (Bonneau et al 2014)

Figure 123 and 124 show the diluate concentrations and power applied to the stack with 103 \(A/m^2\). All chloride and bicarbonate ions were transferred between \(t=0\) and \(t=1\) hour. Sulfate concentration steadily decreases to approximately 2 mg/L (75% passage) over the 2.5-hour experiment. The current density was set at a constant 103 \(A/m^2\) and the voltage was varied. Lower voltage indicates that a lower amount of energy is required for ion passage, whereas a high voltage indicates that a lot of power is required to pass ions across the membrane. Therefore,

Figure 124 indicates once chloride and bicarbonate ions are depleted, it takes more energy to transfer sulfate ions and the passage velocity decreased.
Table 22 compares three different current densities (41, 56, and 103 A/m²) with respect to transfer duration, number of recirculation loops, average power, and energy consumption. The two biggest factors to focus on are average power and energy consumption. While the experiment using 103 A/m² was an hour shorter than the experiment with 41 A/m², more energy is required achieved the same amount of sulfate passage with higher current density. Therefore, it is more effective to use a current density of 56 A/m² with the non-selective membranes to reduce electrical resistance across the membranes, but still achieve good sulfate transfer.

<table>
<thead>
<tr>
<th>Initial current density (A/m²)</th>
<th>Average current density (A/m²)</th>
<th>Transfer duration for 1 mS/cm (min.cm/mS)</th>
<th>Number of recirculation loops for 1 mS/cm</th>
<th>Average power (W)</th>
<th>Energy consumption for 1 mS/cm (J.cm/mS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>41.4</td>
<td>12.00</td>
<td>8.0</td>
<td>1.04</td>
<td>746</td>
</tr>
<tr>
<td>56</td>
<td>56.6</td>
<td>8.85</td>
<td>5.9</td>
<td>1.75</td>
<td>923</td>
</tr>
<tr>
<td>103</td>
<td>56.7</td>
<td>10.92</td>
<td>7.3</td>
<td>5.18</td>
<td>3385</td>
</tr>
</tbody>
</table>

*Information is borrowed from Dutch reports indicating that the convention in this report is different than in the US so (,) is used instead of ()
D.2 Additional Information: Non-Selective Membrane Comparison

Table 23 outlines the parameters of the three types of membranes compared: Fujifilm, MEGA, and PCCell.

**Table 23: Main characteristics of membranes used (Bonneau et al 2014)**

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Thickness (μm)</th>
<th>Electrical resistance (Ω cm² 0.5M NaCl)</th>
<th>pH stability</th>
<th>Membrane type</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>FUJIFILM AEM-Type II</td>
<td>160</td>
<td>5</td>
<td>2-10</td>
<td>Homogeneous a.e.m</td>
<td>-</td>
</tr>
<tr>
<td>FUJIFILM CEM-Type II</td>
<td>160</td>
<td>8</td>
<td>4-12</td>
<td>Homogeneous c.e.m</td>
<td>-</td>
</tr>
<tr>
<td>MEGA AM(H)-PES</td>
<td>750 (swelled)</td>
<td>7.5</td>
<td>0-10</td>
<td>Heterogeneous a.e.m</td>
<td>Quaternary ammonium</td>
</tr>
<tr>
<td>MEGA CM(H)-PES</td>
<td>700 (swelled)</td>
<td>8</td>
<td>0-10</td>
<td>Heterogeneous c.e.m</td>
<td>Sulfonic acid</td>
</tr>
<tr>
<td>PCCELL PC Acid 100 PEEK</td>
<td>80</td>
<td>-</td>
<td>0-10</td>
<td>Homogeneous a.e.m</td>
<td>Quaternary ammonium</td>
</tr>
<tr>
<td>PCCELL PCSK</td>
<td>160-200</td>
<td>2.5</td>
<td>0-11</td>
<td>Homogeneous c.e.m</td>
<td>Sulfonic acid</td>
</tr>
</tbody>
</table>

The non-selective membrane comparison study was performed on two types of brine: raw IEX regenerant (brine) from the Andijk III facility and brine that has been pretreated with monoselective membranes. The concentrate and diluate flow rate was 13 L/h, and the electrolyte flow rate was 175 L/h. The current density applied in the ED stack 105 A/m² with a maximum of 10 V (2 V per cell pair) to treat 2 L of IEX regenerant. The concentrate solution had an initial concentration of 2.5 g/L NaCl and the electrolyte solution had a concentration of 5 g/L NaCl. A 35 mL sample was collected every 5 mS/cm decrease to analyze sulfate, chloride, and bicarbonate concentration.
D.2.1 Study Results and Discussion

PCCell, Mega, and Fujifilm non-selective membranes were compared with respect to ion depletion, conductivity of treated brine, ion speed of transfer, NOM passage, and energy consumption. Figure 125 shows the percentage of ion depletion and difference in conductivity for each membrane raw brine. This figure indicates PCCell can transfer chloride and bicarbonate the best (95% Cl⁻/85% HCO₃⁻). However, PCCell is not good at transferring sulfate (45% depletion). Mega membranes are the most efficient at transferring sulfate (75% ion depletion), and perform average in transferring chloride and bicarbonates (80% Cl⁻/50% HCO₃⁻ depletion). Finally, Fujifilm has a high sulfate transfer in raw brine (90% ion depletion), and average transfer of chloride and bicarbonate (90% Cl⁻/63% HCO₃⁻ depletion). Additionally, all three membranes performed equally with respect to the difference in conductivity.

![Figure 125: Comparison per ion and per membrane of the a) ion depletion in percentage in the raw brine and b) difference in conductivity (Bonneau et al 2014)](image_url)
Figure 126 shows the percentage of ion depletion and difference in conductivity for each membrane brine after stage 1. This figure indicates PCCell can transfer chloride and bicarbonate the best (100% Cl\(^-\)/90%). However, PCCell does not perform well at transferring sulfate (30% ion depletion). Mega membranes are the most efficient at transferring sulfate (80% ion depletion), and average at transferring chloride and bicarbonate (90% Cl\(^-\)/73% HCO\(_3^-\) depletion). Finally, Fujifilm has the worst performance with respect to ion depletion of chloride, bicarbonate and sulfate (68%, 23%, and 23%, respectively). Mega and PCCell membranes were able to reduce the conductivity the most (12 mS/cm and 8 mS/cm, respectively), whereas Fujifilm performed the worst at reducing conductivity with only a 4 mS/cm reduction.

\[\text{Figure 126: Comparison per ion and per membrane of the a) ion depletion in percentage and b) difference in conductivity in the brine after stage 1 (Bonneau et al 2014)}\]

Figure 127 compares each membranes performance again in terms of ion depletion and by speed of ion transfer for the raw brine. Again, PCCell membranes shows to be most efficient in reducing chloride concentration, Mega membranes for reducing sulfate concentration, Fujifilm
membranes are average in reducing all ion concentrations. Figure 127 also suggests that the speed of ion transfer is very similar for each membrane type. (approximately 1.40 meq.cm\(^2\).h\(^{-1}\)).

**Figure 127: Comparison per ion and per membrane of a) ion depletion in meq.cm\(^2\) and b) the speed of transfer in the raw brine (Bonneau et al 2014)**

Figure 128 compares each membranes performance in terms of ion depletion and by speed of ion transfer for the raw brine. Mega membranes perform the best with depletion the greatest amount of ions (5 meq.cm\(^2\)); PCCell membranes are the second most efficient in ion depletion (3 meq.cm\(^2\)); and Fujifilm is the least efficient with only a 2 meq.cm\(^2\) ion depletion. Figure 128 indicates the speed of ion transfer is very similar for each membrane type (approximately 1.40 meq.cm\(^2\).h\(^{-1}\)).
Figure 128: Comparison per ion and per membrane of a) ion depletion in meq.cm-2 and b) the speed of transfer in the brine after stage 1 (Bonneau et al 2014)

Figure 129 compares the NOM passage across each membrane type. PCCell only transfers 3% of NOM, Mega transfers 15% and Fujifilm transfers 29%. Therefore, this suggests that PCCell performs the best with respect to NOM retention in the diluate stream.

Figure 129: Comparison of NOM passage (Bonneau et al 2014)
Figure 130 compares the energy consumption of each membrane type for raw brine and brine after stage 1. The energy consumption to treat raw brine is similar across all types of membrane, roughly 45 – 51 Wh.eq\(^{-1}\), with PCCell membranes requiring the least amount of energy, and Mega/Fujifilm membranes requiring slightly more energy. However, the energy required to treat the brine after stage 1 varied a bit more – Mega membranes required the least amount of energy (45 Wh.eq\(^{-1}\)); PCCell needed slightly more (55 Wh.eq\(^{-1}\)); and Fujifilm required the most amount of energy (63 Wh.eq\(^{-1}\)).

Figure 130: Comparison of energy consumption per brine and membrane (Bonneau et al 2014)

### D.3 Additional Information: Impact of Concentrate Conductivity

This study was conducted with two concentrate concentrations to treat raw Andijk III IEX brine. The first concentrate solution was 60 L of pure RO water (ROW), and the second was 60 L of 18g/L NaCl solution. These trials were run in batch with a diluate and concentrate flow of 520
L/h and electrolyte flow of 750 L/h. The electrolyte solution was a 5% sulfamic acid solution. A 35 mL sample was collected every 2-3 mS/cm decrease to analyze sulfate, chloride, and bicarbonate concentration. The experiment was stopped when the diluate conductivity reached 15 mS/cm.

D.3.1 Study Results and Discussion

The concentrate concentration study shows a comparison of ion depletion in the diluate stream, NOM passage, current utilization, and energy consumption. Figure 131 compares the ion depletion achieved by using the two concentrate solutions. Chloride and bicarbonates were the only two ions that were transferred from the diluate into the concentrate. The trial with ROW concentrate suggests 21.2 meq/cm² Cl⁻ and 3.4 meq/cm² HCO₃⁻ was transferred, whereas the NaCl solution suggest 21.4 meq/cm² Cl⁻ and 2.8 meq/cm² HCO₃⁻ was transferred. No sulfate ions were transferred in either trial.

![Graph showing ion depletion](image)

*Figure 131: Comparison of ion depletion per ion and concentration, meq.cm⁻² (Lebon et al 2014)*

Figure 132 compares the current utilization in each trial. The current utilization in the ROW experiment for chloride was 76%, bicarbonate was 12%, and “others” was 12%. The current
utilization in the NaCl experiment for chloride was 82%, bicarbonate was 11%, and “others” was 7%. This report does not define the components that make up the “others” category.

![Figure 132: Comparison of current utilization per ion and per concentrate (Lebon et al 2014)](image)

The speed of ion transfer of chloride was 12 meq/h for the ROW concentrate and 10 meq/h for the NaCl concentrate. The bicarbonate speed of ion transfer was the same in both experiments. NOM passage in experiment with ROW concentrate was 1.5%, and 3.8% for the experiment using the NaCl concentrate. The energy consumption in the trial ROW trial was 55 Wh/meq, whereas 45 Wh/meq was required for the NaCl concentrate.
APPENDIX E: ION CONCENTRATION DATA
Table 24: HWL Data, Batch Pilot Study

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<th>Date</th>
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<th>Bicarbonate mg/L</th>
<th>Sodium mg/L</th>
<th>NOM mg/L</th>
<th>Sulfate mg/L</th>
<th>Conductivity mS/m</th>
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Ion passage per membrane area is an indication of membrane performance because as membrane resistance increases, less ions will pass across the membrane per area. Figure 133 shows ion passage during both batch experiments. The data presented in *Figure 133* suggest membrane performance with respect to ion passage per membrane area does not significantly decrease over time.

*Figure 133: Ion Passage per Membrane Area, Batch Experiments*

*Figure 134* shows the average ion passage for each target ion with variation of 1-standard deviation away from the mean. This data shows the ion passage per membrane area of sulfate is insignificant when compared to the high ion passage of both chloride and bicarbonate ions. This is comparable to the prior study conducted by Bonneau et al 2014 and Lebon et al 2014, discussed in Section 2.3.
Figure 134: Average Ion Passage per Membrane Area, Batch Experiments
APPENDIX F: DEMINERALIZATION TEST DATA
### TRIAL NUMBER: 1

#### PROJECT: PWNT

**DATE:** 3/10/2016

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<th>pH</th>
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**Average:**

0.54 | 0.00%   
0.53 | 2.86%   
0.53 | 5.03%   
0.59 | 7.51%   
0.58 | 30.85%  

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<th>Temperature (°C)</th>
<th>pH</th>
<th>Brine Conductivity (mS/cm)</th>
<th>Temperature (°C)</th>
<th>pH</th>
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<th>Brine Pressure (bar)</th>
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APPENDIX G: SUPPORTING DOCUMENTS, SPACER FOULING

CELL APPARATUS DESIGN
The spacer fouling cell unit would ideally consist of one ED membrane on the bottom of the Teflon spacer and one spacer in the rectangular opening of the Teflon spacer, such that the spacer would be flush up against the top block and flow would only pass through the spacer (Figure 21 and Figure 22). However, the thickness of the Teflon spacer is more than double the size of one spacer. Four options were proposed to alter the cell unit:

1. Use the existing Teflon spacer and cut the spacer/membranes to fit exactly inside the spacer. With this option, there will be a spacer, anion exchange membrane, spacer, and cation exchange membrane layered in that respective order. The thickness of the four layers is approximately the same as the Teflon spacer.

2. Order a more flexible material (rubber or silicon) < 1 mm and press the membrane/spacer to the upper cell part. This will take time to order/arrive at KWR.

3. Order a newly developed cell unit with a section to enclose the membrane/spacer by rubber rings. This will take some time to design, order, and arrive at KWR.

4. Try to use kit (caulk) to seal off the membrane/spacers inside the Teflon spacer. This method will be messy and take time to clean once each trial is complete.

Table 25 shows the results of three trials testing Option 1: two with brine and one with tap water. All trials were run at speed 2.5 with recirculation of the brine/tap water. The first trial was completed with brine. The membranes and spacers were cut as close as possible to the shape of the Teflon spacer, however, a challenge of getting the spacers and membranes correctly sized is the uneven shape of the rectangle opening. The edges on the inside of the Teflon spacer are not straight, so much time is spent trying to get the ED spacer/membrane to fit exactly (about two and
a half hours to get the two sets of membranes and spacers cut). The pressure in this trial increased roughly 0.07 bar over the two hours of operation and with minimal leakage.

The second trial was run with a new set of membranes/spacers using just tap water to compare the two runs. At the beginning of this trial, the pressure was 0.62 bar and then stabilized to about 0.58 bar. Then, after about 20 minutes, the pressure decreased to 0.55 bar, upon which it stayed constant for the rest of the trial. Again, this trial also had minimal leakage.

The third was operated with the same spacers as in trial two (tap water). The pressure was high (0.83 bar, possibly due to air bubbles) compared to the start of the previous runs. Then, after about 5 minutes the pressure stabilized to 0.58 bar, and only increased 0.01 bar for the duration of the trial.

These trials suggest that reproducibility cannot be achieved for Option 1 with the design of the cell unit as is. These results show that the pressures of Trial 1 and 2 do not have similar patterns when brine is used as the operational fluid. However, this difference might be due to the fact that the spacers/membranes were not changed after running water through the cell unit. This might be true due to the results from the first two trials 18-19 February, which both showed 0.05 – 0.1 bar increase over time using the SIX® brine and ED membranes/spacers.

In summary, there are three challenges for Option 1:

1. Time spent on cutting membranes exactly same size as Teflon spacer
2. Precision of cutting to avoid channeling
3. Some leaking occurs

Table 25: KWR Results, Option 1 Trials

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<th>Fluid</th>
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Option 2 was tested using the existing transparent cell unit with silicon spacers instead of the Teflon spacer. In order to test this set-up, red dye was used to track the flow path. The first few trials were conducted with water to prevent a bloody mess of red dye. The red dye was equally dispersed throughout the length and width of the ED spacer. Figure 135 shows the trial with red dye flowing through the spacer unit. Trials were also run with ED spacers cut to a larger width, but as the area of spacer under the silicon increased, the amount of leakage increased.

![Figure 135: KWR SPS Trial with Red Dye](image)

Three trials were run with similar sized spacers as in Figure 135, replacing the spacer each time. There was no leaking of the red dye outside of the spacer for the first two trials. There was a
very small amount of dye that leaked outside of the spacer area in the third run, but no dye leaked outside of the cell unit. The challenge here is that it will be very difficult to identify small leakage points when using the SIX® brine due to its lighter color. Therefore, if no brine is leaking out of the sides of the cell unit, the leak will not be detected.

The ED cell was tested with silicone rubber spacer and SIX® regeneration brine (see Table 1 for results). The first trial began at 0.83 bar and resulted in a slight pressure increase of 0.15 bar. Then, the system was flushed with water, opened, and the ED spacer/membrane pair was replaced with a new pair to test the reproducibility. The pressure increased beyond 1 bar in the first few seconds, so the bolts were loosened slightly to bring the pressure back to roughly 0.85 bar to begin the trial. There was only 0.02 bar increase for the duration of the trial (1.5 hour). The system was flushed again with water and a new pressure gauge was attached – electronic with digital reading from the computer.

The modification of using a thinner silicon spacer instead of the Teflon is definitely an improvement. The new, electronic pressure gauge is also an improvement to the cell, both of which are advantageous. However, the main challenge with this unit is the possibility of an unknown leak. The next objective is to complete a particle size distribution of the SIX® regeneration brine to classify what is actually in the brine for an understanding of the applicability of this test unit.

Option 3 proposed designing a new cell to achieve the desired goal of measuring how many particles get stuck in the spacer and how long it will take to clog the ED spacer. A technologist at KWR drew a potential design of this new cell which is similar to the existing except there is space for a rubber O-ring to direct the flow and minimize channeling across the full length and width of the ED spacer. The size of this cell is still under discussion because the overall goal is to relate this
test to how particles move throughout the spacer on full-scale. If the cell unit was designed to the full size of an ED spacer, the minimum length to width ratio could not be achieved (5:1) – the spacer size is 500 x 300 mm. However, the manufacturing of the ED spacers includes a rubber gasket along all four sides of the spacer with distributors. The challenge here is the schedule and cost of a cell that can hold the full-sized spacer.
APPENDIX H: SUPPORTING DOCUMENTS, SEM AND EDX EXPERIMENTS
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Electron Image 2

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Electron Image 5

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APPENDIX I: ADDITIONAL INFORMATION ON PH ADJUSTMENT OF BRINE
I.1 Additional Information: Impact of Altering the pH of NS Stage Brine

In order to determine the volume of HCl required to achieve pH 5 the following titration of 1 L of brine was used (Figure 136). It took 6.84 mL of 10% HCl to achieve pH 5, therefore, 1300 mL of 10% HCl was used to reduce 190 L of treated brine to pH of 5.

![Titration: Brine from Stage 1](image)

**Figure 136: Titration for Adjusting pH of Brine**

Figure 137 shows current density versus diluate conductivity of the two trials. The higher the current density to diluate conductivity ratio is, the better the stack is performing. Therefore, this data shows that the diluate under normal pH conditions is operating more effectively than that of diluate with low pH. This suggests that the membranes do not perform well under lower pH conditions because membrane resistance increases.
Figure 137: Diluate Conductivity and Current Density, EDNS pH Adjustment Experiment
APPENDIX J: AOC AND BPP RESULTS
## J.1  AOC Results, Brine Desalinated with Electrodialysis

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**MONSTER OF PAN-P1-BRINE-DS-ONV**

**Kolf A van 27-07 tot 28-07 op tafel gestaan. Iv**

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**Max:** 3,1E+06

**Var.:** 748,780 216,667 965,447 953,354 1,79
### AOC Results, Brine Desalinated with Electrodialysis, Diluted 100 Times

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**Notes:**
- **Max. Kve/mL:** 9,3E+03
- **Max. Kve/mL:** 9,0E+04

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**Notes:**
- **Max. Kve/mL:** 7,8E+03
- **Max. Kve/mL:** 1,0E+05

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<th>µg AOC nox</th>
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**Rounded to: 2,085 7,917**

**Kolf: 5,6 ml**

**Verd. Factor: 99,95**
### BPP analyse rekenblad

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Max. BP$_2$ 3.930 ng/L St.dev. 0.397 ng/L V.C. 10.1%
BPC$_{14}$ 47.786 d.ng/L St. dev. 0.686 d.ng/L V.C. 1.4%

### Opmerkingen:

Ingevoerd door: 
Geautoriseerd door: 
Datum: 
Datum:

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## J.4 BPP Results, IEX Pilot Brine

### BPP analyse rekenblad

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Max. BP$_y$ = 1436.163 ng/L  
St.dev. = 99.237 ng/L  
V.C. = 6.9 %

BPC$_{14}$ = 13063.647 d.ng/L  
St. dev. = 1163.826 d.ng/L  
V.C. = 8.9 %

### Opmerkingen:

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Ingevoerd door:  
Geautoriseerd door:  
Datum:  
Datum:

O:\Bacteriologie\CHECKLISTEN en berekeningen MICRO\BPP  
Versie 1.2 16092016
### BPP analyse rekenblad

#### Samplenumber
970597

#### Monstercode
PAN-IX-BRJN

#### Monsterdatum
10/5/2016

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Max. BP$_F$ 590.989 ng/L St.dev. 47.281 ng/L V.C. 8.0%

BPC$_{14}$ 7461.774 d.ng/L St. dev. 495.430 d.ng/L V.C. 6.6%

---

**Opmerkingen:**

05-10-2016 Verdunningsfactor 20 gemeten.

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**Ingevoerd door:**

**Geautoriseerd door:**

**Datum:**

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### BPP analyse rekenblad

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<th>BP7 (ng/L)</th>
<th>Gemiddelde St.dev.</th>
<th>BPC14 (d.ng/L)</th>
<th>Gemiddelde St.dev.</th>
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**Max. BP7** 10647.053 ng/L  St.dev. 72.740 ng/L  V.C. 0.7%

**BPC14** 123732.182 d.ng/L  St. dev. 32742.826 d.ng/L  V.C. 26.5%

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**Opmerkingen:**
05-10-2016 Verdunningsfactor 100 gemeten
W.1 gemiddelde van dag 4 is hoger dan gemiddelde van dag 7

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*Ingevoerd door:* Geautoriseerd door:

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