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Protocols for Electrodialysis

**Membrane selection,
Membrane fouling
and Design**

Protocols for Electrodialysis. Membrane selection, Membrane fouling and Design

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Preface

Spent regenerate streams from anion exchange (AIX) processes are rich in natural organic matter (NOM) and salts, and are formed during the implementation of this technology. Recently, new initiatives consider these streams as a resource for regeneration salts and fertilizers (NOM). At Vitens the well-known HumVi technology using nanofiltration (NF) is exactly aiming at this; and the HumVi process is recently implemented at full-scale in Spannenburg.

The HumVi technology could not directly be employed at Andijk III because of the presence of sulphates in the spent AIX regenerate of PWN. An alternative was found in double electrodialysis (ED) treatment recovering regeneration salts and a potential fertilizer (NOM). The so-called TKI NOMixed was successfully constructed together with project partners PWN, PWN Technologies and KWR, and was awarded by RvO. The TKI NOMixed project aimed at developing tools to support the full-scale ED design for the treatment of spent AIX regenerate streams from Andijk III.

The project was carried out in close collaboration with the project partners, without whom this project would have been impossible. I am very grateful for the support, many interactions and suggestions from Elisabeth Vaudevire (PWNT), Bram Martijn (PWNT) and John Boogaard (PWN). Furthermore, my direct colleagues Luc Palmen (KWR), Wolter Siegers (KWR), Hendrik van Beverloo (KWR) are acknowledged for their indispensable help in respectively project management, flow cell measurements and particle counting measurements. Not to forget my colleagues from the workshop: Harry van Wegen (KWR) and Sidney Meijering (KWR). Students who worked on ED generated many useful data and brought interesting issues to the discussion table. I am grateful for the work and assistance of Jérémy Bonneau, Thibault Lebon and Katerina Messologitis. Furthermore, more from the 'outside' many people contributed to this work, such as ED suppliers (people from GE, IEC, Eurodia, Fuji, PCA and PCCell), universities (Jan Post, Walter van der Meer and Geert-Jan Witkamp) and other KWR departments (Annemieke Kolkman, Dennis Vughs).

I hope that this report reflects a little bit the commitment of all these people. And I sincerely hope that this report contributes to the understanding of ED on full-scale for the treatment of spent AIX regenerate streams.

Emile Cornelissen

July 20, 2016

Summary

In 2014 PWNT designed, built and operated a new water treatment system at Andijk III which uses an innovative anion exchange (AIX) process (SIX®). A spent AIX regenerate stream is produced during AIX, which is concentrated in NOM and salts and is challenging to discharge or to process. The treatment of the spent AIX regenerate with consecutive mono-selective and non-selective electrodialysis (ED) membranes is investigated. This report provides additional support for the design of a full-scale installation for the ED treatment of spent AIX regenerate, and more specifically providing supporting protocols for (i) ED membrane selection, (ii) ED fouling and (iii) ED design.

ED membrane selection is based on (i) ED membrane characterization and on (ii) ED process performance comparison. A pre-selection of different ED membranes can be made on the basis of available ED characterization data, while in the next phase pre-selected ED membranes should be experimentally compared in an ED performance comparison study. On the basis of ED membrane characterization, the best available ED membranes are expected to have a high ion-exchange capacity (and therefore high swelling degree), a low membrane resistance and a high permselectivity for the relevant anions and/or cations. Characterization data is easily accessible, independent of ED application, available for a single ED membrane, but is usually incomplete (or lacking), dependent on applied methods and time-consuming to obtain. On the basis of ED process performance comparison, the most efficient ED membrane(s) (pairs) should display a high ion transport (rate), a high transport number, a high specific permselectivity (e.g. chloride relative to sulphates) and a high current utilization. Performance parameter data is specific and includes practical issues (e.g. fouling), but is limited to specific circumstances, limited in gaining understanding and only provides ED membrane info in pairs. The effect of NOM on the ED performance was found to be important, which should be evaluated using an appropriate ED testing protocol, e.g. the IEX/PCCell laboratory scale ED set-up or six compartment ED cell.

ED membrane fouling (particulate fouling, biofouling, organic fouling and scaling) during ED processes can result in a decrease of the diluate flow (due to clogging of the feed spacer), an increase of the electrical resistance, a permselectivity decrease and a membrane modification. Particulate fouling appeared to be a dominant fouling mechanism during ED on raw spent anion exchange regenerate at PWNT in Andijk, and a systematic ED fouling approach was proposed to relate the presence of particulate material in feed water to a hydrodynamic pressure loss at constant feed flow in a representative flow cell. A change in particle size distribution after passing the flow cell was related to an increase in pressure drop, which was attributed to entrapment/precipitation of particles in the flow channel corroborated with visual observations. A systematic research plan was proposed focusing on selection of the (i) pre-treatment system, (ii) feed spacer configuration and (iii) ED membrane type (in relation to fouling).

An ED design approach was suggested by conducting a limited set of experiments and measurements in function of a given feed water quality and a desired product water quality. The optimal operational set point of the ED plant depends on the variables: (i) membrane type, (ii) ED stack design (hydraulic conditions) and (iii) flow rate which determine the limiting current density I_{\max} . From this the membrane cost and desalination and pumping

energy cost of the ED installation can be estimated. This design approach was different from the design procedure of Eurodia which was based on maximum voltage.

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1 Introduction

1.1 Background

In 2014 PWNT designed, built and operated a new water treatment system at Andijk III which uses SIX® technology (an innovative anion exchange (AIX) process) and Ceramac® (an innovative ceramic microfiltration process). Removal of natural organic matter (NOM) using AIX leads to many different advantages for downstream processes.

A spent AIX regenerate stream is produced during AIX, which is concentrated in NOM and salts and is very difficult to discharge or to process. From a previous BTO project concerning possible routes for regenerate treatment, the use of electrodialysis (ED) seemed to be very promising (BTO 2014.054). From short lab-scale experiments it was found feasible to separate the spent AIX regenerate solution with ED into a salt solution which can be reused as a regeneration liquid and into a NOM-rich solution with an added value as a fertilizer. It is unknown if this concept is viable on a larger scale for a longer duration.

PWNT is investigating the long term operation of a pilot ED to treat the spent AIX regenerate streams from the SIX® process which will provide experience and design parameters for the design of a full-scale ED installation for spent AIX regenerate treatment. Specifically collaboration in the fields of ED membrane selection, ED membrane fouling and ED design additional support is required as was defined in the TKI NOMixed project.

1.2 Research goals

Provide collaboration for the design of a full-scale installation for the ED treatment of spent AIX regenerate, and more specifically provide supporting protocols for (i) ED membrane selection, (ii) ED fouling and (iii) ED design.

2 ED membrane selection

This chapter covers the selection of ion-exchange or electrodialysis (ED) membranes¹. Two approaches for ED membrane selection can be distinguished which can be combined and compared based on (i) ED membrane characterization experiments (section 2.1) and/or reported data (section 2.2) and (ii) ED process performance comparison (section 2.3). Both approaches are covered in this chapter and will be discussed (section 2.4) and evaluated for practical application (section 2.5).

2.1 ED membrane characterization

The effectiveness and performance of ED processes depends strongly on the properties of the ED membranes, being either anion-exchange membranes (AEM) or cation-exchange membranes (CEM). Different AEM and CEM membranes are characterized by the following parameters (Strathmann, 2004):

Material properties

- Mechanical stability
 - Membrane thickness
 - Swelling degree (water content)
 - Water permeability
 - Tensile strength
- Wettability by contact angle measurements
- Zeta-potential measurements
- Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS)

Electrochemical properties

- Ion-exchange capacity
- Electrical membrane resistance or conductivity
- Permselectivity

Different characterization parameters for ion-exchange membranes will be described below.

2.1.1 Materials properties

The mechanical stability of ED membranes involves the measurement of the membrane thickness, swelling degree (related to water content), water (or hydraulic) permeability and tensile strength (Strathmann, 2004). The *tensile strength* and elastic deformation data of ED membranes is obtained from a stress versus strain diagram (Garcia-Vasquez et al, 2013) (see Figure 2.1). The stress versus strain curves usually consists of three regions: (i) elastic deformation at low strain (linear part of the curves in Figure 2.1), (ii) plastic deformation at higher strain (non-linear part of the curves in Figure 2.1) and (iii) breakage at a certain high strain (related to burst strength) (final parts in the curves in Figure 2.1). The mechanical properties of the membranes usually depends strongly on the water content, and the mechanical stability should therefore be assessed using either dry membranes or membranes which are conditioned under standard conditions with solutions used during practical application.

¹ Ion permeable membranes used in electrodialysis are essentially sheets of ion-exchange resins. They usually also contain other polymers to improve mechanical strength and flexibility.

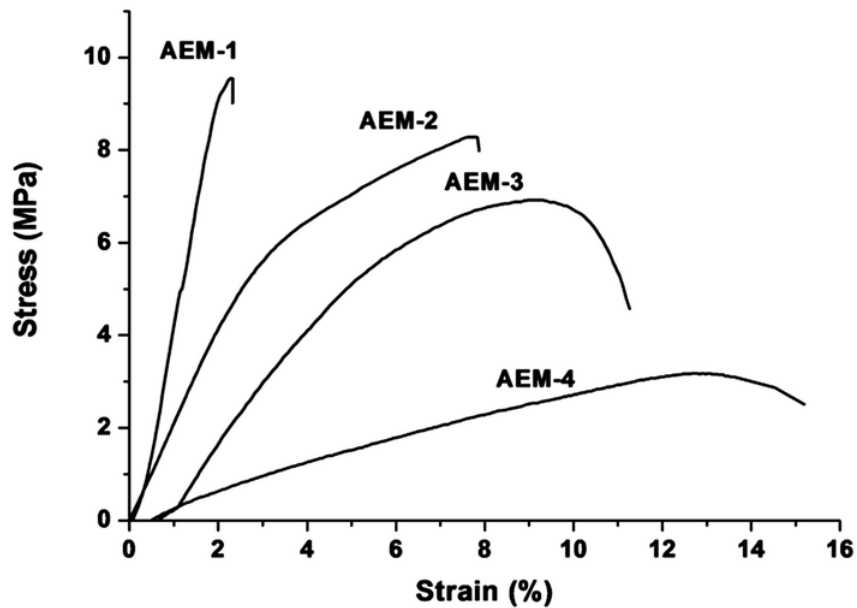


FIGURE 2.1 TYPICAL STRESS VERSUS STRAIN CURVE FOR ED MEMBRANES

The *membrane thickness* can be determined with electronic equipment devised for plastic film thickness measurements. Thickness is related to the mechanical strength of the AEM and CEM membranes, and is related to the electrical resistance (Vanoppen et al 2015, Bazinet and Araya-Farias, 2005).

The *swelling degree* (related to water content) determines the mechanical stability, the electrical resistance, the permselectivity and the water permeability. The swelling degree depends on the membrane material, type and concentration of ion-exchange groups, counter ions and cross-linking density (Strathmann, 2004). Furthermore, the swelling degree and water content depends on the composition of the solution in contact with the ED membrane. Many sophisticated methods are used to determine the water content and structures in AEM and CEM membranes, such as differential scanning calorimetry (DSC), infrared spectroscopy (IRS) and nuclear magnetic resonance (NMR). The disadvantage is that only a small membrane area can be investigated, which is especially relevant for heterogeneous ED membranes. Usually the water content is determined by measuring the weight difference between a wet and dry ED membrane. The water content is determined after equilibration for at 24 hours with deionized water or another test solution (after removing excess water from the membrane surface). Then the membranes were dried at 50°C for at least 24 hours. The swelling degree (wt.%) can be determined by:

$$wt\% \text{ swelling} = \frac{W_{wet} - W_{dry}}{W_{wet}} \cdot 100 \quad (1)$$

In which W_{wet} and W_{dry} are the weight of membrane sample in the wet and the dry state. This weight can be determined using precision scales (Vanoppen et al, 2015) or using thermobalances (Garcia-Vasquez et al, 2013).

The *water permeability* is determined using hydraulic pressure provides information about diffusive and convective transport through the membrane in function of hydraulic pressure (Strathmann, 2004). Usually this effect is negligible compared to transport due to electrodialysis. However, membrane defects can cause a higher water permeability. Therefore this parameter is used as a quality control measurement.

The wettability of solid surfaces is a very important property and is governed by both the chemical composition and geometrical microstructure of the surface. The polymers used to make ED membranes differ in their polarity and can yield either hydrophobic or hydrophilic membranes. Membrane hydrophobicity can be altered as a result of adsorption of organic matter and formation of biofilms. The hydrophobicity of a surface is defined through the measurement of a contact angle between a surface and a droplet of a fluid. Contact angle can be measured in a number of different analytical methods, one of which is the captive bubble contact angle measurement that uses an air bubble immersed in a liquid (under the membrane) instead of a liquid droplet on top of the membrane. Yet, the most common method to measure contact angles is the sessile drop technique where the angle, contact radius, and the height of a sessile drop on a solid surface is viewed from its edge through an optical microscope. Computerized goniometer systems combining digital optics and shape recognition programs can more accurately measure the contact angle in both the captive bubble and sessile drop methods. Contact angle measurements can typically be performed at laboratories performing surface characterization, e.g. at research groups on material science or colloidal science, e.g. Wetsus, TU Delft and UT in the Netherlands.

The selectivity of a ED membranes is governed by electrostatic interactions occurring between charged solutes and the charged membrane surface. The characterization of the surface electrical properties of ED membranes is important to understand and predict their behaviour. Measurement of membrane surface potential can be performed by three available methods including streaming or zeta potential, electrophoresis, and titration. Only the first method is discussed here. The gap cell used for measuring zeta potential of ED membranes is described in literature (Sabbatovskii et al., 2016). It is similar to that applied in the Anton Paar SurPass 3 electrokinetic analyser, which was employed by Yaroshchuk and Luxbacher (2010) for measuring external and internal (inside membrane pores) zeta-potential, as well as by Sedkaoui et al. [50], who developed a promising method for determining the lateral conductivity of ED membranes from the measurements of the streaming current and streaming potential. Zeta potential measurements can be performed at Anton Paar (thomas.luxbacher@anton-paar.com).

A number of microscopic techniques are typically employed for characterization of membrane roughness, microstructure, and morphology and can be employed for ED membranes. These techniques provide important information for (i) understanding and improving membrane properties, and (ii) characterizing and analysing membrane fouling. The two most commonly used techniques for examining membrane fouling, surface structure and morphology, are atomic force microscopy (AFM) and scanning electron microscopy (SEM). Atomic force microscopy is used to measure membrane surface roughness and it provides morphological images by scanning a nanometer-scale sharp tip over a surface. It has become an important characterization tool of imaging the surface of ED membranes at up to the atomic level resolution (Tan and Bélanger, 2005). Scanning electron microscopy provides direct observation of a sample, including membrane morphology and fouling layer. Very high magnifications and high resolution can be obtained. The SEM can easily be combined with an energy-dispersive X-ray spectroscope (EDS), which enables analysis of elemental composition of the spot being imaged by the SEM. SEM-EDS is often used as a combined tool that can provide detailed information on the size, shape, structure, and chemical composition of membrane material and foulants (Ghalloussi et al, 2015, Zuo et al, 2014). SEM-EDS may also be used to characterize very thin fouling layers, such as microbiological fouling, membrane scaling, or membrane degradation and defects. Conventional SEM often requires sample preparation, such as coating with a thin layer of gold, carbon, or other material in order to reduce membrane surface charge. SEM and AFM can typically be performed at laboratories performing surface characterization, e.g. at

research groups on material science or colloidal science, e.g. Wetsus, TU Delft and UT in the Netherlands.

2.1.2 Electrochemical properties

The ion-exchange capacity is an important parameter for charged membranes which affects all other membrane properties. The ion-exchange capacity is a measure for the number of fixed charges per unit weight of dry polymer, expressed in mmol/g or meq/g. It is determined by titration of the fixed ions using NaOH or HCl. The procedure is explained in Garcia-Vasquez et al (2013). Counter-ions were forced to transfer to a determined solution with the purpose of titrating them. Samples of 10 cm² were immersed into 0.1 M HCl (the counter-ion is Cl⁻) for 2 hours, then rinsed in ultrapure water and immersed in 1 M HNO₃ for at least 12 hours. The chloride content was determined immediately after this time. Samples were finally vacuum dried at 40°C for 24 hours to determine the dry mass (Garcia-Vasquez et al 2013). The range of ion-exchange capacity for commercial ED membranes is typically 1-3 meq/g. A high ion-exchange capacity relates to effective ED membranes.

The electrical membrane resistance (R_m) of ion-exchange membranes (or reciprocal conductivity) is important for the energy requirement of ED processes. In most practical cases the membrane resistance is much lower than the resistance of the dilute solution. It is usually expressed as membrane area resistance in $\Omega \cdot \text{cm}^2$. The electrical membrane resistance is determined by the ion-exchange capacity and the mobility of the ions within the ED membrane matrix (Strathmann, 2004). It can be determined by direct current (DC) or alternating current (AC) measurements. Typically by using a cell with electrodes of known surface area separated by a fixed distance (typically 1 cm). The resistance is measured in the flow cell using a known solution (typically 0.5 M NaCl) with (R_{m+s}) and without (R_s) the membrane positioned between the electrodes (Vanoppen et al 2014). Bazinet and Araya-Farias described the following method in which the electrical membrane resistance was determined in a specially designed cell (conductivity clip) from La Laboratoire des Matériaux Echangeurs d'Ions (Créteil France) with a distance between electrodes of 0.5 cm. The clip ends were immersed in a 1 N NaCl reference solution with the jaws wide apart for 1 min, while the platinized electrodes fixed on each jaw were submerged. The conductance of the reference solution (G_s) was measured with a conductivity meter. Next the membrane was equilibrated for 10 min in the reference solution and then introduced between the clip jaws and the conductance (G_{m+s}) was measured. The electrical membrane resistance R_m was calculated from $1/G_{m+s} - 1/G_s$ (Bazinet and Araya-Farias, 2005). The electrical conductivity (κ) can be determined from:

$$\kappa = \frac{\Delta x}{R_m A} \quad (2)$$

In which κ is the electric conductivity (S/cm), Δx is the membrane thickness (cm), R_m the electrical membrane resistance (Ω) and A is the electrode area (cm²). A low electrical membrane resistance is preferable for ED membranes.

The permselectivity (α) of an ion-exchange membrane is defined as the ratio of the flux of specific components to the total mass flux through the membrane at a given driving force (Strathmann, 2004). The permselectivity of an ion-exchange membrane, i.e. its charge selectivity is determined by the concentrations of counter and co-ions in the membrane, which depends again on the ion-exchange capacity and the ion concentrations of the outside solutions (depends on Donnan exclusion). The permselectivity can be determined by the ratio of the measured membrane potential difference (ΔV_m) and the theoretical membrane potential difference (ΔV_t), when using a standard salt in which the cation and the anion have approximately equal transport numbers, such as KCl.

$$\alpha = \frac{\Delta V_m}{\Delta V_t} \quad (3)$$

Measurement of the membrane potential difference across an ion-exchange membrane is carried out in a static experiment separating two electrolyte solution of different concentrations (Vanoppen et al, 2015). In a static experiment water transport through the ion-exchange membrane due to electro-osmosis and osmosis is not taken into account, and only the apparent permselectivity is determined. The theoretical membrane potential difference (ΔV_t) follows from the Nernst-equation by:

$$\Delta V_t = \frac{RT}{F} \ln \left(\frac{a_c}{a_d} \right) \quad (4)$$

With R the universal gas constant (J/mol.K), T the absolute temperature (K), F the Faraday constant (C/mol), a_c and a_d the chemical activity of the concentrated and diluate solution (-) and ΔV_t the theoretical membrane potential difference (V). Using KCl at 0.5 M and 1.0 M in different well mixed chambers in a static experiment at 25°C, the theoretical membrane potential difference is 0.0158 V. A high permselectivity is preferable for ED membranes.

2.2 Membrane selection on the basis of reported ion exchange properties

Different ED technology suppliers were identified on the basis of literature research and internet search engines (see Table 1).

TABLE 2.1 MAIN MANUFACTURERS OF ION-EXCHANGE MEMBRANES (VALERO ET AL, 2011)

Manufacturer	Country	Commercial brand
Asahi Chemical Industry Co.	Japan	Aciplex
Asahi Glass Col. Ltd	Japan	Selemin
DuPont Co.	USA	Nafion
FuMa-Tech GmbH	Germany	Fumasep
GE Water & Process	USA	AR, CR,...
Fujifilm	Japan	E-separation membrane
LanXess Sybron Chemicals	Germany	Ionac
MEGA a.s.	Czech Republic	Ralex
PCA GmbH	Germany	PC
Tianwei Membrane Co.Ltd	China	TWAED
Tokuyama Co-Astom	Japan	Neosepta

Some of these ED technology suppliers were contacted within the framework of the NOMixed project. The following ED system suppliers were invited to PWNT (Andijk) or to KWR (Nieuwegein) to present their company and their products:

- GE Water & Process (mr. Arnoud Nauwelaerts) Wed 17th Sept 2014 @ 11:00-12:30
- IEC (mr. Tom Thijssen) Wed 24th Sept 2014 @ 14:00-16:00
- Eurodia (mr. Gérard Guérif) Mon 10th Nov 2014 @ 13:30-18:30
- Fujifilm (Mr. Jeroen van Nunen) Wed 29th April 2015 @ 14:00-16:30
- PCA/PCCell (mr. Altmeijer) Mon 28th Sept 2015 @ 13:00-17:00

ED system suppliers sometimes produce their own ion-exchange membranes (Fuji, Mega,...), while other companies only provide ED systems (IEC/PCCell) and collaborate with ED membrane manufacturers (PCA). A wide variety of ED membrane types are available on the market (Table 2.1). From a selection of literature, internet search and supplier data sheets several materials properties (thickness, swelling) and electrochemical properties (ion-exchange capacity, electrical membrane resistance and permselectivity) were found for

different ED membranes and summed up in Table 2.1. On the basis of these properties suitable ED membranes can be selected. An efficient ED membrane is expected to consist of (i) a high ion-exchange capacity, (ii) a low electrical membrane resistance and (iii) a high permselectivity (Strathmann, 2004). The materials properties such as thickness and swelling degree will determine these properties, e.g. the thickness is expected to inversely correlate with the electrical membrane resistance.

TABLE 2.2 MATERIAL AND ELECTROCHEMICAL PROPERTIES OF ION EXCHANGE MEMBRANES FROM SUPPLIER DATA SHEETS AND LITERATURE

Membrane	Material properties		Electrochemical properties			Reference
	Thickness [mm]	Swelling [wt.%]	Ion-exch. cap. [meq/g]	Resistance [$\Omega \cdot \text{cm}^2$] 1N NaCl	Permselect. [%]	
Asahi ASV-mono	0.11	-	-	3.07	96	Agc.co.jp
Asahi ACS-mono	0.121	-	-	4.39	94	Agc.co.jp
Eurodia ACS	-	20-30	1.4-2	2-2.5	-	Jaime-Ferre et al, 2008
Eurodia ACM	-	15	1.5	4-5	-	Jaime-Ferre et al, 2008
Eurodia AHA	-	13-20	0.5-3	3-5	-	Jaime-Ferre et al, 2008
Eurodia AMX	-	25-30	1.4-1.7	2-3.5	-	Jaime-Ferre et al, 2008
Eurodia CMB	-	37-42	2.4-2.7	-	-	Jaime-Ferre et al, 2008
Fuji A	0.123	-	-	0.93	89	Fujifilmmembranes.com
Fuji A-mono	0.124	-	-	1.1	91	Fujifilmmembranes.com
Fuji AEM (manual)	0.16	-	-	3.5	95	Vanoppen et al, 2015
Fuji CEM (manual)	0.16	-	-	6.1	96	Vanoppen et al, 2015
Fuji AEM (meas.)	0.148	14	-	2.7	94	Vanoppen et al, 2015
Fuji CEM (meas.)	0.17	18	-	3.7	-	Vanoppen et al, 2015
Mega AM(H)-PES	-	-	-	-	-	Dydo, 2012
Mega CM(H)-PES	-	-	-	-	-	Dydo, 2012
PCA PC acid 100	0.08	18	0.4-0.6	-	-	data sheet / Jaime-Ferrer 2008
PCA PCSK	0.18	9	-	2.5	-	data sheet / Dydo 2012
Tokuyama AMX	0.134	-	-	2.35	90	Tokuyama.co.jp
"	0.12-0.18	-	1.4-1.7	2.3-3.5 ²	-	Kabsch-Korbutowicz, 2011
Tokuyama CMX	0.18	-	-	2.5-3.5	-	Xu et al, 2005
"	0.14-0.2	-	1.5-1.8	2.5-3.5	-	Kabsch-Korbutowicz, 2011
Tokuyama CMS	0.155	-	-	1.5-2.5	-	Xu et al, 2005
Tokuyama CMH	0.26	-	-	10-20	-	Xu et al, 2005
Tokuyama AMH	0.27	-	-	11-13	-	Xu et al, 2005
Tokuyama AMX-SB	0.155	23	2.2	-	-	Garcia-Vasquez et al, 2013

Not a single reference reports the complete set of materials and electrochemical properties and several properties of many ED membranes remain unknown (Table 2.2). Therefore, a selection of efficient ED membranes only on the basis of an incomplete data set of materials and electrochemical properties from literature, internet and supplier information is not possible. Nonetheless, potentially interesting ED membranes include Fuji membranes with a low electrical membrane resistance, thin PCA ED membranes and Eurodia membranes with a high ion-exchange capacity.

² 0.5 N NaCl

Although a rough membrane pre-selection can be based on reported materials and electrochemical membrane properties, additional membrane characterization is recommended using the actual feed water. This will be discussed in the following section.

2.3 Membrane selection from practical ED operation

The performance of ion-exchange membrane separation processes depends not only on the membrane properties or the feed and product solution composition, it is also determined by several process and equipment design parameters, e.g. the stack construction (cell geometry, spacer configuration), the feed flow velocities, the current density, the applied voltage to achieve the current density and the residence time of the feed and concentrate solution in the stack. The impact of all these parameters on ED performance follow from a material balance of the entire mass transport in the stack. The mass transport (section 2.3.2) and the membrane selectivity (section 2.3.3) are important parameters to determine the performance of ion-exchange membrane processes in practice. In any practical electrodialysis process not all the current flowing through the stack is used for desalting the feed solution. The so-called current utilization need to be determined (section 2.3.4). The energy consumption is another important parameter in electrodialysis, and is covered in Chapter 4. First a resistance in series approach is discussed to determine the membrane resistances experimentally.

2.3.1 Resistance in series approach

In electrodialysis the applied voltage is linked to the current density, which is rather complex for multi-component solutions at high ion concentrations. Therefore, the following assumptions are made (Strathmann, 2004):

- Ion migration through membranes occurs only due to potential difference;
- The potential difference is constant over the length of the ED membrane;
- The resistance of the solutions and the current density changes over the length;
- Cross-flow is only due to convection (diffusion is extremely small);
- The membranes are strictly permselective;
- Concentration changes due to diffusion of ions, osmosis and electro-osmosis are expressed in the current utilization;
- Concentration changes due to boundary effects are neglectible.

As a first estimation the current density through a cell pair is expressed in function of the solution and membrane properties, the cell dimensions and the applied voltage:

$$i = \frac{V}{\frac{d(C_s^d + C_s^c)}{\Lambda_s C_s^d C_s^c} + R_{m,a} + R_{m,c}} \quad (5)$$

In which V is the applied voltage, d is the thickness of the diluate/concentrate cell, C_s is the salt concentration, Λ_s is the molar conductivity of the solution, $R_{m,c}$ and $R_{m,a}$ are the resistances of the cation and anion-exchange membrane. The superscripts d and c refer to the diluate and concentration.

This equation can be used to determine the membrane resistances experimentally. Firstly, anion and cation-exchange membranes are characterized in pairs during a normal ED experiment. To determine the individual membrane resistance values several ED experiments need to be conducted using different combinations of anion and cation-exchange membranes. Secondly, the solute resistance term $\frac{d(C_s^d + C_s^c)}{\Lambda_s C_s^d C_s^c}$ usually has a higher resistance than the membrane resistances, especially when the product is highly desalinated. This results in an inaccurate determination of the membrane resistances. Finally, the current density in practical ED is limited due to concentration polarization and ion depletion at the membrane

surfaces in the diluate cell. The limiting current density is determined by the stack geometry and the solution flow velocity (see Chapter 4).

2.3.2 Mass transport in ED

In electrodialysis ions are transported from the diluate compartments to the concentrate compartments. The degree of desalination can be expressed by a material balance between the feed, the concentrate and the diluate solutions. The degree of desalination (and concentration of the feed solution) is given by the difference between the feed and product solution ($c_{s,0}^{dc} - c_s^{dc}$), which is in many ED installation identical to the difference between the feed and the brine solution ($c_s^{Cc} - c_{s,0}^{Cc}$). The concentration differences are related to the material balances which takes the volume flow rates in the diluate and concentrate cells and the electric current passing through the stack following:

$$(c_{s,0}^{dc} - c_s^{dc}) \cdot Q^{dc} = (c_s^{Cc} - c_{s,0}^{Cc}) \cdot Q^{Cc} = \frac{\eta I}{\sum_i z_i \nu_i F} \quad (6)$$

Where c is the salt concentration, I is the total current, η is the current utilization, z is the valence, ν is the stoichiometric coefficient, F the Faraday constant, Q^d and Q^c are the flows of the diluate and concentrate solutions. The superscripts d and c refer to the diluate and concentration. The subscripts s , 0 and i refer to total salt solution, inlet solution and anion- or cation. The current is the product of the current density (i) and the total membrane area (A).

Membrane selection during practical ED experiments can be carried out by comparing different anion and cation-exchange membrane pairs using the same set-up and feed solutions under the same operational conditions. Multi-component mass transport will take place when using realistic feed solutions, such as a spent anion-exchange regenerate stream which makes a comparison difficult. An approach which can be followed is targeting and comparing the transport of a single component. Mass transport of a single component can be evaluated by:

$$\Delta m_i^d = m_{i,0}^d - m_i^d = (c_{i,0}^d - c_i^d) \cdot V^d \quad (7)$$

Where m is the mass of the anion or cation (g), c is the concentration of the anion or cation (g/L) and V is the volume of the diluate vessel. The superscript d refers to the diluate and the subscripts 0 and i refers to the inlet solution and anions or cations. Mass transport of different anions and cations during ED with different ion-exchange membranes can be compared to each other while keeping other parameters the same, such as ED set-up and design, feed solution and process parameters. This approach, however, will not provide a thorough understanding of the reasons for mass transport differences between different membranes.

Similarly the rate of the transfer of the different anions and cations can be compared to each other. For an efficient mass transport of anions and cations the rate of transport is important, which will differ among different ED membrane pairs. The rate of transport of a single component can be evaluated by:

$$\frac{\Delta m_i^d}{t} = (c_{i,0}^d - c_i^d) \cdot Q^d \quad (8)$$

Where m is the mass of the anion or cation (g), c is the concentration of the anion or cation (g/L) and Q is the flow of the diluate solution. The superscript d refers to the diluate and the subscripts 0 and i refer to the inlet solution and anions or cations. Mass transport rate of different anions and cations during ED with different ion-exchange membranes can be

compared to each other while keeping other parameters the same, such as ED set-up and design, feed solution and process parameters. This approach, however, will not provide a thorough understanding of the reasons for mass transport rate differences between different membranes.

2.3.3 Membrane selectivity in ED

Feed solutions treated by electrodialysis usually contain more than one electrolyte, particularly in the case of spent regenerate solutions from AIX resins which contain high concentrations of chlorides, sulphates, carbonates and natural organic matter. The membrane selectivity or permselectivity of ED membranes is determined by the ratio of the flux of a single component to the total mass flux through the membrane at a given driving force. The flux of an anion or cation is defined as:

$$J_i = \frac{dc_i V}{dt A} \quad (9)$$

Where J_i is the ion flux, c_i the concentration of the ion, V is volume and A the membrane area. In ion-exchange membranes the current is carried preferentially by the counter-ions, i.e. anions by cation-exchange membranes and cations by anion-exchange membranes. The fraction of the current which is carried by a single component, either anion or cation, is expressed by the ion transport number and given by (Strathmann, 2004, Güler et al, 2014):

$$T_i = \frac{z_i J_i}{\sum_i z_i J_i} \quad (10)$$

Where T_i is the (ion) transport number of a single component, J_i is the anion or cation flux and z_i is the valence. The sum of the transport numbers of all ions in a solution is 100%. The transport numbers of different components of the same charge can differ strongly as a result of the size and properties of the components and the structure of the membrane. The selectivity of an ion-exchange membrane is determined by the concentrations of the counter and co-ions in the membrane, which strongly depends on the ion-exchange capacity of the ED membrane (section 2.1.2).

The permselectivity between two components i and j is the transport number of a single component i relative to component j , and is also referred to as the relative permselectivity (Sata, 2000, Güler et al, 2014). It is defined as:

$$P_j^i = \frac{T_i/T_j}{c_i/c_j} \quad (11)$$

Where T_i and T_j are the transport numbers of single components i and j , and c_i and c_j is the concentration of i and j at the membrane surface in the diluate side.

2.3.4 Current utilization or current efficiency in ED

In practical ED processes the current flow is not completely used for desalting the feed solution. An incomplete current utilization is caused by different factors including, (i) imperfect selective ED membranes, (ii) current leaking through the stack manifold, (iii) water transport due to osmosis and electro-osmosis and (iv) water splitting phenomena which utilizes current. Usually the latter term can be neglected, resulting in three terms which determine the total efficiency of the current utilization. The three utilization terms depend on many factors including transport numbers of single components and ion-exchange membranes, water transport numbers of the membranes, number of cell pairs, etc. To determine the total current efficiency all these factors need to be known, which requires extensive membrane characterization efforts.

A more operational approach is to determine the current efficiency from the ratio between the ion transport and the total applied current. Rearrangement of equation 6 will provide the current efficiency (Strathmann, 2004; Zhang et al, 2011):

$$\eta = \frac{z_i(c_{i,0} - c_i) \cdot Q \cdot F}{I \cdot N} \quad (12)$$

Where η is the current efficiency, z is the valence of a single component, c_i is the concentration of a single component, Q is the flow rate, F is the Faraday constant, I is the current through the stack and N is the number of cell pairs. The current efficiency can be calculated for single components (anions and/or cations) to calculate the contribution to the transport of this component. The summation of the transport of all the anions and cations will indicate the total ion transport and is usually <100%. The rest of the current utilization is linked to the previously mentioned factors, imperfect selectivity, current leakage and water transport.

2.3.5 Power and energy requirement for ion transport

The required electrical power for desalting a solution is determined by the total current through the ED stack multiplied by the applied voltage. Using this formula the power requirement can be calculated for desalination of a spent regenerate during a laboratory or pilot scale experiment. The power requirement of one cell pair follows from (Strathmann, 2004):

$$P = V \cdot I \quad (13a)$$

Where P is the power requirement, V is the applied voltage and I is the total current. By multiplication of the power requirements for one cell pair with the operational time and the number of cell pairs in the stack the energy required for desalination follows from:

$$E = N \cdot V \cdot I \cdot t \quad (13b)$$

Where E is the energy requirement, N is the number of cell pairs, V is the applied voltage, I is the total current and t is the operational time. Using formulas (13a) and (13b) the power and energy requirement can be calculated during an experiment.

2.3.6 Power and energy requirement for pumping

In ED recirculation pumps are required for sufficient diluate and concentrate flow. The role of the pumps is to provide enough pressure to overcome the operating pressure to move water at a required flow rate. The operating pressure of the system is a function of the flow through the system and the friction experienced in the flow channel (e.g. hydraulic diameter, type of spacers,...). The hydraulic pump power can be calculated by:

$$P = \frac{Q \cdot \rho \cdot g \cdot h}{3.6 \cdot 10^6} \quad (14)$$

Where P is the hydraulic pumping power (kW), Q the flow rate (m^3/h), ρ the density (kg/m^3), g the gravity constant ($9.81 \text{ m}/\text{s}^2$) and h the pump head (m). From this the pumping energy can be calculated, since the hydraulic pump power is the amount of energy consumed per unit time ($E = P \cdot t$).

2.4 Membrane selection – a discussion

For the design of a ED desalination plant for the treatment of spent anion exchange regenerate streams, a robust membrane selection procedure is important. The ED membrane will also determine the ion transport, the rate of ion transport and permselectivity of the different anions and cations in the spent AIX regenerate stream. These properties will ultimately contribute to the current efficiency and therefore to the power and energy requirement for such an ED process. Membrane selection is essential for the design of an ED installation. Many ED suppliers and ED products are available, and a rational approach is important to select the best available ED membrane for the specific purpose of the ED process. Two approaches for ED membrane selection can be distinguished which can be combined and compared based on (i) ED membrane characterization experiments and/or data and (ii) ED process performance comparison. Both approaches were covered in this chapter and will be discussed briefly below.

ED membrane characterization parameters for membrane selection can be subdivided into material properties (e.g. mechanical stability, membrane thickness, swelling degree and water permeability) and electrochemical properties (e.g. ion-exchange capacity, membrane resistance and permselectivity). These data can be found in scientific literature, from internet search engines and from supplier data sheets. The advantage is that most of the available characterization data is (usually) obtained from controlled laboratory methods and is independent of the specific ED application. When this data is reported in scientific literature it is easily accessible and obtained from independent sources. On the basis of reported characterization data a pre-selection of available ED membranes can be made. Another advantage is that characterization is carried out on a single membrane, either anion exchange or cation exchange membranes. The disadvantage of the ED characterization approach is that the data is usually incomplete, and especially characterization data for new(er) ED membranes are lacking. Even when characterization data is accessible, it is sometimes questionable if data from different sources can be compared because different experimental set-ups and methods might be used. In any case, the obtained characterization data should be treated with care. In the case that characterization data is not available, ED characterization parameters should be determined experimentally. This usually requires specific set-ups and methods which are very time consuming (section 2.5). In short obtaining/determining ED characterization data for ED membrane is very valuable, but the data should be treated critically since characterization is not always standardized.

ED performance comparison for membrane selection is a very specific method to obtain the best available ED membrane. Parameters to evaluate an ED experiment using actual feed solutions, e.g. spent anion exchange regenerate, include ion transport, rate of ion transport, ion transport number, specific (perm)selectivity and current utilization. From an ED experiment also the power and energy requirement for ion transport can be determined as is covered above (section 2.3). The advantage of membrane selection using ED performance comparison is that membrane selection is targeted specifically at the relevant ED application. It does not use data from literature which might be difficult to validate. The ED performance comparison method also includes the effects of membrane fouling (see chapter 3) on the ED performance which cannot be determined straightforward from ED membrane characterization. The disadvantage is that the approach is limited to the specific circumstances during the ED experiment, and that variations in feed composition, process conditions and design might result in different ED performance results potentially affecting ED membrane selection. Another drawback is that this method is also relatively time consuming, because ED membranes are studied always in pairs (alternating anion and cation exchange membranes). To characterize a single anion and cation exchange membrane, different ED membrane combinations need to be made, tested and evaluated. Finally,

because of different phenomena occurring at the same time (e.g. concentration polarization, fouling, spacer clogging and ion transport) the fundamental understanding is limited compared to a determining ED characterization parameters from laboratory methods which tend to be more systematic. In short, ED performance comparison for membrane selection is very valuable, but limited in scope and fundamental understanding.

An ED testing protocol should contain both approaches (e.g. ED membrane characterization and ED performance comparison) for ED membrane selection. A pre-selection of different ED membranes can be made on the basis of available ED characterization data. Best available ED membranes are expected to have a high ion-exchange capacity (and therefore high swelling degree), a low membrane resistance and a high permselectivity for the relevant anions and/or cations. Water permeability (osmosis and electro-osmosis) should be low and thickness coupled to mechanical stability should be sufficient. Some of these parameters are counteracting and compromises should be made. Lacking ED membrane characterization data should be determined experimentally, for an adequate pre-selection. In the next phase pre-selected ED membranes should be experimentally compared in an ED performance comparison study. This can be carried out on laboratory scale using the same ED set-up using the same ED cell design (e.g. equal membrane area), the same feed spacers³, the same operational parameters and the same feed solution. Since ED membranes are operated in pairs, different combinations of anion and cation exchange membranes should be made to evaluate the performance of single ion-exchange membranes. The most efficient ED membrane(s) (pairs) should display a high ion transport (rate), a high transport number, a high specific permselectivity (e.g. chloride relative to sulphates) and a high current utilization. This should translate into a low power and energy requirement (for ion transport) for the most effective ED membrane(s) (pairs) for the specific ED application. To gain more fundamental understanding, ED membranes can be characterized using standard set-ups and methods before and after ED application. It is expected that fouled ED membranes will display different characterization parameters.

In the TKI NOMixed project membrane selection studies were already performed on laboratory and pilot ED scale on the basis of an ED process performance comparison. Bonneau et al (2014) investigated the ion transport rate, permselectivity and current utilization (power and energy requirement) for both mono-selective and nonselective PCCell membranes. This in a performance comparison study using an IEC/PCCell laboratory scale ED set-up. High current efficiencies and selectivities were found for chloride and the effect of natural organic matter was found to be beneficial for ion transport due to an additional membrane resistance. Lebon et al (2015) investigated different ED membrane types (PCCell, Fujifilm and Mega) in the same IEC/PCCell laboratory ED set-up, and compared ion transport rate, permselectivity and current utilization (power and energy requirement). The Mega ED membranes performed best regarding ion transport rate and current utilization, but the NOM transfer to the concentrate side was highest. The effect of NOM on the ED performance was found to be significant in both studies, and for an ED testing protocol the effect of the presence of NOM should be evaluated. This can be done by comparing a synthetic spent AIX regenerate solution only consisting of anions and cations with the actual spent AIX regenerate solution (Bonneau et al, 2014). Another approach is designing a synthetic spent AIX regenerate solution including a standard type of NOM solution, e.g. using Swansea River Humic Acid (SRHA) solutions. The drawback of this last approach is that a standard type of

³ Membrane performance is influenced by the type of feed spacer. The thickness of the diluate/concentrate cell is given by d in equation 5. Thicker feed spacers will negatively influence the current density at a fixed applied voltage. The feed spacer design will also influence the turbulence in the diluate/concentrate channels and influence the limiting current density (see chapter 4). In performance comparison studies it is recommended to use the same type of feed spacers.

NOM solution might not be representative to the actual NOM present in the spent AIX regenerate stream. It might be advisable to take and store a large sample of actual spent AIX regenerate and treat this as a standard solution.

2.5 Practical directions and protocols for membrane selection

As was discussed ED membrane selection is based upon two approaches (i) ED membrane characterization and (ii) ED process performance (section 2.4). The membrane selection procedure is based upon a general approach, while in this section practical directions and protocols are discussed specifically for the PWN case in Andijk III for the ED treatment of spent AIX regenerate. This section is based on personal communication with Jan Post on 18th February 2017.

For a practical and applicable approach to ED membrane selection at the Andijk III pilot facility, a small laboratory ED set-up is recommended to test ion transport rate, permselectivity and current utilization using different preselected ED membranes. Preselection is based on data sheets provided by ED suppliers and on literature characterization data (sections 2.2 and 2.4). A typical suitable ED set-up for ED membrane performance testing is the IEC/PCCell laboratory scale ED system as used and described by Bonneau (2014). In this set-up different ED membranes can be tested in which particularly the anion-exchange membrane is of interest because of a more pronounced membrane fouling (section 3.1). The details of the IEC/PCCELL laboratory scale ED system are provided by Bonneau (2014) and Lebon (2015) and are not described in this report.

More elaborate ED membrane characterization tools are being developed in the Netherlands by research groups at the UT and Wetsus. Typically ED membranes are characterized in specialized equipment under standard conditions using deionized water with 0.5 M NaCl. Using this type of equipment, ED membranes can be characterized and grouped between good and poorly performing ED membranes based on properties such as ion transport rate, permselectivity and current utilization. Nevertheless, this characterization strategy does not provide a guarantee for ED operation under practical conditions with real feed water (e.g. spent AIX regenerate) for which they are not necessarily representative. ED membrane characterization in specialized laboratories will typically provide not more than an indication for a suitable ED membrane in practice. A typical example is the six compartment ED cell to determine the electrical membrane resistance which was used by Galama et al (2014) and Dlugolecki et al (2010). The measuring set-up was made from plexiglass and consisted of six separate compartments. The central membrane, which was the membrane under investigation, was either a cation or an anion exchange membrane. The other four membranes were auxiliary ion exchange membranes produced by Mega (Czech Republic). In both compartments adjacent to the membrane under investigation a 0.5 M NaCl solution was used. The second and fifth compartment contained the same solution to avoid influences of the electrode reactions at the working electrodes. The conductivity of the solution close to the membrane under investigation were continuously monitored to ensure a constant composition during a set of experiments. The voltage drop over the membrane under investigation at different current densities was measured using Haber-Luggin capillaries. The final resistance was given by the slope of the current density versus voltage drop curve. To obtain the pure membrane resistance, this combined resistance had to be corrected for the resistance of the solution, which could be determined from a blank experiment without a membrane. More details about their set-up and protocol can be found in Galama et al (2014) and Dlugolecki et al (2010). The method is rather labour some and is very sensitive.

More fundamental methods to determine ED characteristics include the development of simple 2D models to understand ED membranes on a molecular level by using the Nernst-

Planck equation not only in the flow channels but also in the membranes (Tedesco et al, 2016). Models require as only input parameters the geometrical features of the system, the membrane charge density, and the diffusion coefficients of ions in the channel and in the membrane. Membrane properties such as permselectivity are calculated as outputs of the model, and depend on position in the channel.

3 ED membrane fouling

This chapter first covers the topic of ED fouling and fouling control as obtained from literature in respectively section 3.1 and section 3.2. A standard ED particulate fouling approach is presented together with a proof of principle based on a first experiment followed by planned experiments and specific recommendations for the standard ED fouling test (section 3.3). Other ED fouling approaches are discussed and compared (section 3.4).

3.1 Fouling during ED

In practical applications of ED processes the feed water composition is usually very complex containing different components, such as suspended and colloidal matter and dissolved organic and inorganic compounds⁴. The presence of these components will influence the ED process in different ways resulting (usually) in a loss of ED performance. Fouling during ED processes can result in a decrease of the diluate flow (due to clogging of the feed spacer), increase of the electrical resistance (current drop at a fixed potential difference), decrease migration yield (permselectivity decrease) and membrane modification (Bazinet and Araya-Farias, 2005). Generally four types of fouling can be identified: particulate fouling, biofouling, organic fouling and scaling (Table 3.1). These four fouling mechanisms will occur probably simultaneously on pilot scale resulting in a difficult individual fouling observation. It is recommended to derive a (selection of) method(s) to characterize the dominant fouling type in order to implement an effective pre-treatment method.

Particulate fouling includes the precipitation of suspended or colloidal matter (e.g. silicates, calcium carbonate particles, iron hydroxide flocs) occurring at the entrance and within the flow channels of the ED stacks resulting in an increase in hydrodynamic pressure losses (Vermaas et al, 2013) and non-uniform flow distribution in the ED stack (Strathmann, 2004, Grossman and Sonin, 1972). Precipitation can also occur onto the membrane surface which can result in an increase of the electrical resistance of the stack and might even lead to damage of the ED membranes. Especially the present organic acids can precipitate onto specifically anion exchange membranes and cause a strong increase in the membrane resistance (Korngold et al, 1970). This is also considered as an effect of particulate fouling.

Biofouling is caused by attachment and growth of bacteria on the feed spacer and on the membrane surface. In ED this phenomenon can lead to clogging of the feed spacer resulting in an increase in hydrodynamic pressure losses and non-uniform flow distribution in the ED stack (Post, 2009). Because most of the bacteria are negatively charged, they can potentially adhere to the anion exchange membranes. In recent research, adhesion of bacteria onto ED membranes did not result in an increase of the electrical resistance (Vasalbehagh et al., 2016). In another study using microbial fuel cells biofouling was found to impact the permselectivity (Ping et al, 2013). Furthermore, the topic of biofouling in ED is virtually unexplored, which is expected to play a role in ED processes.

⁴ ED is used in the food industry, e.g. wine industry and dairy treatment in which specific foulants play a role, such as humic and fulvic acids (in wine treatment) and biopolymer and fatty acids (in dairy treatment). For these applications different type of ED membranes are used with a different lifetime expectancy than in ED in (waste)water treatment. This report focuses, however, on ED in wastewater treatment.

Organic fouling occurs when organic compounds such as macromolecules, polyelectrolytes and organic anions such as humates and surfactants interact with ED membrane surfaces⁴. Organic acids such as humates can precipitate/adsorb specifically onto anion exchange membranes and cause a strong increase in membrane resistance (Korngold et al, 1970). Other organic molecules which were found to foul ED membranes were aromatic and aliphatic organics (Tanaka et al, 2012), pesticides (e.g. endosulfan) (Banasiak et al, 2011), organic acids (Xu et al, 2012), humic substances (Lee et al, 2002) and anionic surfactants (Lindstrand et al, 2002a, Lindstrand et al, 2002b). Organic anions which are small enough and have a low electro mobility can virtually remain in the ED membrane structure and cause a drastic increase in the membrane resistance. This phenomenon is also known as membrane poisoning and can occur with certain detergents. Membrane poisoning is difficult to control and should be avoided. Anion exchange membranes are most sensitive to organic and particulate fouling (Vermaas et al, 2013).

Scaling occurs when sparingly soluble salts enter the ED stack and form insoluble salt which can precipitate onto the membrane and particularly the feed spacer. Well-known scalants are CaCO_3 , CaSO_4 , BaSO_4 , SrSO_4 and SiO_2 which form an additional resistance layer on top of the ED membranes. The solubility of these salts in water at 20°C is $S(\text{CaCO}_3) = 13 \text{ mg/L}$, $S(\text{CaSO}_4) = 2.6 \text{ g/L}$, $S(\text{BaSO}_4) = 2.5 \text{ mg/L}$, $S(\text{SrSO}_4) = 0.13 \text{ g/L}$ and $S(\text{SiO}_2) = 0.12 \text{ g/L}$. Scaling can occur both on anion and cation exchange membranes resulting in an increase in electrical resistance of the membranes and a change in the permselectivity (Korngold et al, 1970). The influence of calcium carbonate scaling was investigated both on anion exchange membranes (Araya-Farias et al, 2006) and on cation exchange membranes (Casademont et al, 2007, Casademont et al, 2008 and Bazinet et al, 2005). It seems to be more severe on cation exchange membranes (Ping et al, 2013).

3.2 Control of ED fouling

Control of ED fouling can be subdivided into (i) pre-treatment, (ii) feed water conditioning, (iii) ED membrane selection, (iv) process control and (v) chemical cleaning. The effectivity of these strategies depend strongly on the specific feed water which determines the type of fouling which occurs (Table 3.1).

Pre-treatment using rapid sand filtration (RSF) or micro- or ultrafiltration (MF/UF) is very effective for the removal of particulate matter (e.g. colloidal and suspended material) which will reduce particulate fouling of ED stacks. RSF and MF/UF pre-treatment can also be effective in reducing the levels of larger organic compounds, such as macromolecules and larger organic anions. Activated carbon filtration (ACF) can be effective in removing organic compounds too, and will reduce organic fouling (and membrane poisoning) and possibly biofouling in ED stacks. Biological activated carbon filtration and sand filtration will consume nutrients to reduce biofouling problems in downstream ED stacks. Other pre-treatment methods include precipitation, flocculation and ion-exchange which tackle different fouling types.

Feed water conditioning includes pH control and addition of additives (e.g. anti-scalants, biocides and bicarbonates). pH control is known to be effective in scaling and particulate fouling control, affecting respectively the solubility of sparingly soluble salts and the particle-membrane interaction. For example, at lower pH (bi)carbonates reacts to CO_2 and calcium carbonate is more soluble and less prone to scale. Addition of anti-scalants (e.g. EDTA) will complex cations, such as calcium or magnesium, resulting in lower Ca/Mg concentrations in the solution and less scaling in the ED stacks. Addition of small quantities of bicarbonates will increase the alkaline buffer capacity of the feed water which may act as a prevention against fouling (Korngold et al, 1970).

ED membrane selection was covered in chapter 2 of this report in relation to operational criteria (e.g. desalination capacity, permselectivity, energy requirement). An additional criterion is the anti-fouling property of the ED membranes, which is very dependent on the feed water quality. ED membrane parameters related to anti-fouling properties include ion-exchange capacity (influencing electrostatic attraction or repulsion), hydrophobicity, surface roughness and membrane structure (section 2.1.1). Because of the complexity of the interactions, ED membrane selection based on ED fouling should be carried out systematically using different ED membranes in parallel with actual feed water. ED membrane selection is particularly relevant for organic fouling and possibly also for biofouling.

Process control to control ED fouling includes many approaches such as lowering the electrical current density or voltage over the stack, decreasing the recovery and increasing the diluate flow rate. Lowering the current density or voltage will reduce the fouling load towards the ED membranes, which can be effective for all fouling types. The disadvantage is of course a lower ion transport, which can be compensated by installing more ED membrane area. Decreasing the recovery will reduce the concentration increase in the ED stack, which will reduce the risk of scaling. Increasing the diluate flow will increase the turbulence in the ED stack and reduce the concentration polarization (see chapter 4), which may reduce all types of fouling. A very effective operating mode is regularly reversing the polarity of the ED stack referred to as electrodialysis reversal (EDR) (Strathmann, 2004). This operating mode is able to remove deposited material from ED membranes and can be effective for all types of fouling. EDR will not be covered extensively in this report.

Chemical cleaning is needed when all the other fouling control strategies appear to be insufficient to retain a stable ED operation. Depending on the type of fouling which occurs in the ED stack (both on the feed spacer and on the membrane surface) a variety of chemical cleaning agents can be effective. For example, acids are effective against scaling, bases and surfactant are effective against organic and particulate fouling and biocides are effective in deactivating biofouling. Important parameters during chemical cleaning are duration, flow rate, chemical composition and concentration. A sufficient flow rate is required to create enough turbulence to remove material from the membrane surface towards the outlet of the ED stacks. This can be achieved by using a high flow rate or possibly by using two-phase flow (air/water cleaning). The last option is a conceptual thought, which is currently not suitable for standard ED stacks.

Another consideration is the effect of ED membrane ageing. As a result of regular chemical cleaning, the ED membranes will age which will result in the loss of ion exchange capacity. Acidic cleaning did not impact the investigated anionic exchange membrane, while alkaline cleaning did result in dehydrochlorination enhanced by the presence of quaternary ammonium groups (Garcia-Vasquez et al, 2016). Regular cleaning cycles resulted in membrane inflate-deflate sequences. Therefore, membrane toughness was deteriorated, thus leading to the formation of cracks and fractures as observed before on the same type of membrane after industrial electrodialysis in which traditional CIP is performed through acid-base sequences (Garcia-Vasquez et al, 2016). In another study they used cation-exchange membranes which suffered from significant degradation; while it was generally more robust and resistant than the anion-exchange membrane. Both cation-exchange and anion-exchange membranes lost a part of ion-exchange sites (Ghalloussi et al, 2015). Ageing has to be considered when designing ED installations.

TABLE 3.1 OVERVIEW OF DIFFERENT FOULING TYPES AND FOULING CONTROL IN ED

type	Description	Position	Foulants	Control	References
Particulate	Agglomeration of suspended solids	Membrane & spacer	SiO ₂ , Fe(OH) ₃ , Al(OH) ₃ , Cr(OH) ₃	MF/UF pre-treatment, pH control, lower recovery, higher flow	6,13
Biofouling	Attachment and growth of bacteria	Membrane & spacer	Bacteria and extra-polymeric substances	MF/UF or ACF or SF pre-treatment, biocides	10,12,13
Organic	Attachment of organic matter	Membrane	Macromolecules, polyelectrolytes, organic anions	MF/UF or ACF pre-treatment, cleaning	2,7,8,9,11,14
Scaling	Precipitation of sparingly soluble salts	Membrane & spacer	CaCO ₃ , CaSO ₄ , BaSO ₄ , SrSO ₄ , SiO ₂	Lower recovery, pH control, anti-scalants	1,3,4,5,7

1.	Araya-Farias et al, 2006	6.	Grossman & Sonin, 1972	11.	Tanaka et al, 2012
2.	Banasiak et al, 2011	7.	Korngold et al, 1970	12.	Vaselbehagh et al, 2016
3.	Bazinet et al, 2005	8.	Lee et al, 2002	13.	Vermaas et al, 2013
4.	Casademont et al, 2007	9.	Lindstrand, 2002a,b	14.	Xu et al, 2012
5.	Casademont et al, 2008	10.	Post, 2009		

3.3 Standard ED particulate fouling approach

3.3.1 Introduction

ED membrane fouling is a complex phenomenon involving different fouling types which occur simultaneously when operating an ED installation using actual feed water (section 3.1). In the case of the spent anion regenerate streams at Andijk of PWNT the feed solution consists of different inorganic and organic components both in suspended and dissolved form, while changing in composition in time. This feed solution will result in different fouling types during ED operation to occur at the same time, possibly even changing in time. A systematic approach is therefore desired to distinguish the effects of one single fouling type during ED operation in order to gain more understanding and to find a direction for ED fouling control.

From ED research at PWNT to obtain the limiting current using raw spent anion exchange regenerate, it became visually clear that particulate fouling appeared (Lebon, 2015). This was furthermore confirmed by a decrease of the diluate flow rate (Lebon, 2015). Particulate fouling seemed to be the most urgent problem operating ED on spent regenerate at PWNT. Other fouling types will take longer to establish (biofouling) or can be easily controlled by pH or recovery adjustment (scaling). Apart from particulate fouling, organic fouling is also expected to have a significant impact on ED operation using spent anion exchange regenerates. It was decided, however, that particulate fouling is the foremost focus of the systematic approach aimed at understanding fouling and finding directions for fouling control in ED.

From observations during ED research it is found that particulate fouling occurs as a result of the presence of suspended and colloidal material in the spent regenerate stream. This material accumulates onto the feed spacer and is largely responsible for the diluate flow decrease (or hydrodynamic pressure loss increase), and probably to some extent also responsible for the increase in membrane resistance due to precipitation onto the membrane surface as a layer with low current conductivity. The objective of this first systematic ED fouling approach is to relate the presence of suspended and colloidal material in the feed water to an increase in the hydrodynamic pressure loss at a constant feed flow rate in a representative flow cell mimicking flow channels in an actual ED stack. Furthermore, the

interaction of suspended and dissolved material in the feed with the ED membrane can also be assessed when representative ED membranes are used. The influence of electric forces occurring in ED is neglected during this first approach, which would otherwise require a more time-consuming approach and an actual ED set-up. The method and set-up will be discussed in more detail in the following section.

3.3.2 Set-up and method for a systematic particulate ED fouling study

The objective of the systematic approach is to observe particle deposition on the feed spacer and possibly on the membrane during a short experiment on lab scale. A flat sheet membrane set-up provided by KWR will be used, in which spent regenerate can be recirculated over the membrane⁵ and feed spacer while pressure drop is monitored at a constant feed flow rate. An increase of the pressure drop will indicate clogging of the feed spacer. One parameter at the time, such as pre-treatment process, membrane type and feed spacer type can be varied to systematically measure the impact on particulate fouling. At the end of the trial, the membrane and feed spacer will be autopsied to quantify and identify the deposition.

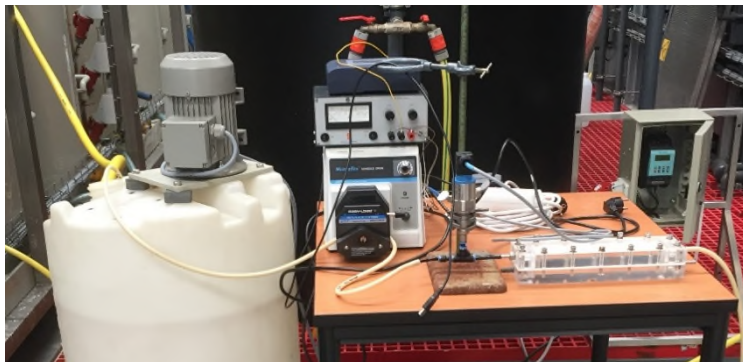
A transparent flow cell is used with a flow channel with the dimensions of a normal spacer ($H \times W \times L = 450 \mu\text{m} \times 39 \text{ mm} \times 240 \text{ mm}$). The flow cell contains an ED membrane (anion or cation exchange membrane) on the bottom side, with a feed spacer present in the flow channel (the permeate channel is blocked to prevent water permeation). Visual observation and high speed camera recording is possible from the feed side (top) of the membrane to observe particle transport and visual fouling of the membrane in time. Feed water from a stirred 1,000 L feed tank is transported to the flow cell using a peristaltic pump (Masterflex L/S variable-speed drive with 10-turn speed control and remote capabilities, 6 to 600 rpm, 230 VAC (Model No. 77521-47)) operated at a constant flow rate⁶ of 10 L/h. The feed pressure is continuously logged (Squirrel data logger Model: SQ2010) using a pressure indicator (Endress & Hauser Cerabar T PMC131) at the entrance of the flow cell. The flat sheet ED membrane flow cell set-up is depicted in Figure 3.1.

Feed water samples will be taken at the entrance and the exit of the flow cell for each test run and analysed on the presence and distribution of particles using a particle counter (Pamas, Water Viewer) (more details in Appendix 1). At the end of each run the ED membrane is investigated and analysed on the presence of active biomass (using ATP measurements) and organic matter (using TOC measurements). Furthermore, SEM pictures will be made to allow a more detailed observation of deposits on the membrane surface. Membrane surface characterization will be carried out at the entrance and exit of the flow cell to obtain information about particulate and organic fouling.

⁵ When more feed water is available re-circulation is not necessary, and once-through flow can be applied

⁶ The feed flow rate was first assumed to be constant, but later it appeared to decrease in time and was measured manually during the experiments

FIGURE 3.1 PHOTO OF THE SET-UP USED FOR FOULING STUDIES

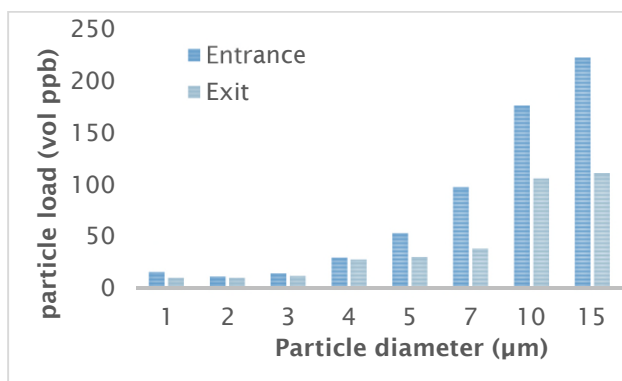


3.3.3 Proof of principle of systematic ED fouling test

For a proof of principle the ED particle fouling test set-up was installed on-site at PWNT in Andijk. A fresh spent anion exchange regenerate sample was taken and fed to the system. The flat sheet cell was loaded with an anion exchange membrane (PCCell PCMVA) and a standard feed spacer (diamond geometry, 26 mil²). Feed water was fed to the flow cell and re-circulated to the feed vessel. The feed water at the entrance and exit of the flow cell was characterized using particle counting on the last day of the run. The pressure drop over the spacer filled flow cell was monitored continuously during 3.5 days of recirculation. At the end of the run a membrane autopsy was performed on the ED membrane on ATP, TOC and SEM inspection (outside the scope of this report).

The presence of suspended and colloidal material in the spent anion exchange regenerate is indicated by particle counting measurements. Particles are measured in the feed water as (median) particle load (in volume ppb) ranging in size between 1 and 15 μm (Figure 3.2). The spent anion exchange regenerate sample contains significantly larger particles ($> 5 \mu\text{m}$) compared to smaller particles ($< 5 \mu\text{m}$). After passing the flow cell the particle load decreases for larger particles ($> 5 \mu\text{m}$), while the particle load remains the same for smaller particles ($< 5 \mu\text{m}$). This could be due to precipitation or entrapment of (larger) particles in the feed spacer channel, onto the feed spacer and/or onto the ED membrane.

FIGURE 3.2 PARTICLE SIZE DISTRIBUTION AT THE ENTRANCE AND EXIT OF THE FLOW CELL

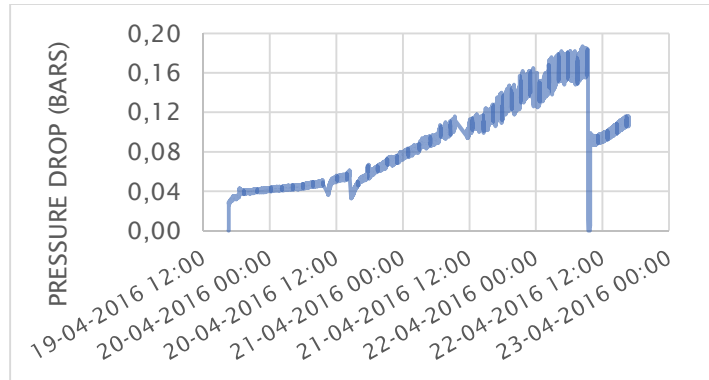


Pressure drop increased steadily in time during flow of spent AIX regenerate through the spacer filled flow cell (Figure 3.3). While the initial pressure drop was approximately 0.04 bar,

⁷ 1 mil = 1/1000 inch

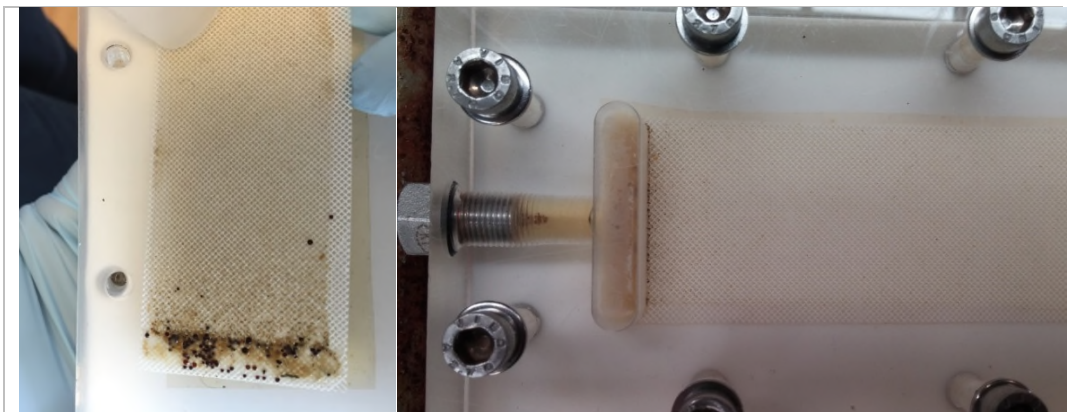
it significantly increased to 0.18 bar during the course of 2.5 days; a more than 4.5 times increase in pressure drop, indicating a severe clogging of the feed spacer channel. This corroborates with findings obtained from the particle counters. On 22-4-2016 at 11:30 the flow through the cell was reversed which caused a sharp drop in the pressure drop.

FIGURE 3.3 TYPICAL PRESSURE DROP VERSUS TIME CURVE FROM ED FOULING EXPERIMENT



From visual observation a distinct clogging of relatively large particles could be observed at the entrance of the flow cell (Figure 3.4 left). Possibly the particles are anion exchange resins which carry over to the spent regenerate stream. Furthermore, a clear discoloration of the membrane can be observed (Figure 3.4 right), as a result of the interaction of organic feed water compounds with the membrane surface. Membrane surface characterization will shed more light upon the specific compounds responsible for the discoloration of the membrane. The results of the membrane autopsy are not reported here.

FIGURE 3.4 VISUAL OBSERVATION INDICATES PARTICLE CLOGGING (LEFT) AND MEMBRANE DISCOLORATION (RIGHT)



The objective to relate the presence of suspended and colloidal material in the feed water to an increase of the hydrodynamic pressure loss at a constant feed flow rate in a representative flow cell was met. Particle counter data from the feed water can be related to the measured pressure loss increase in the flow cell due to spacer clogging, which was corroborated by visual observation. The proposed ED particle fouling approach seems to be a solid method.

3.3.4 Planned tests and recommendations

3.3.4.1 Planned experiments with the ED particle fouling set-up

With the standard ED particulate fouling approach, a systematic research was planned for the selection of the most suitable (i) pre-treatment system, (ii) feed spacer and (iii) ED membrane in relation to particulate fouling. Systematic research focuses on optimal pre-treatment and feed spacer selection using a fixed anion-exchange membrane (PCCell PCMVA).

Several spent AIX regenerate streams with different qualities are available at PWNT, specifically from (i) the Andijk III full-scale SIX® installation, (ii) the pilot SIX® installation and (iii) the pilot SIX® installation after denitrification. Pre-treatment of spent AIX regenerate from the SIX® pilot is carried out with cartridge filters with different nominal pore sizes (Table 3.2). The particle size distribution and the pressure drop behaviour in the ED particle fouling set-up can be assessed and compared for the five different water qualities. The most favourable water quality in combination with the most effective pre-treatment process will consist of a low particle load and will result in a limited or preferably no pressure drop increase in the ED particle fouling set-up. The outcome of this systematic research approach will assist in selecting the water type (before or after denitrification) and the pre-treatment (none, 5 µm cartridge filtration, 1 µm cartridge filtration or extensive pre-treatment such as MF/UF). The outcome will, however, depend on the type of feed spacer which is another focus of the systematic research.

Different feed spacers can be used in ED stacks to alter the hydrodynamic conditions in the feed flow cell to influence the particle clogging behaviour. Thick feed spacers are known to decrease feed spacer clogging, but will also influence the ion transport during ED. When the spacer thickness increases the distance between the anion exchange and cation exchange membranes increases, which leads to lower current densities at a constant voltage (equation 5). Lower current densities will result in a lower ion transport or a lower degree of desalination (equation 6). To maintain an equal ion transport when using thicker spacers, higher potential differences (voltage) should be used, which requires more electric energy (equation 14). This research is focused on particle fouling, however, the effects on the electric energy should be evaluated in the total ED design. Three feed spacer types are selected, characterized as (i) standard spacer (0.71 mm or 28 mil), (ii) thick feed spacer (0.86 mm or 34 mil) and (iii) thin feed spacer (0.51 mm or 20 mil) (Table 4). The flow cells are fed by spent AIX regenerate from the SIX® pilot without pre-treatment. The most favourable feed spacer (most probably the thicker feed spacer) will result in a limited or preferably no pressure drop increase in the ED particle fouling set-up. The outcome of this systematic research approach will assist in selecting the most effective feed spacer in relation to particle fouling.

TABLE 3.2 PLANNED EXPERIMENTS FOR A SYSTEMATIC PARTICLE FOULING RESEARCH (WITH PCCELL PCMVA)

Exp.nr.	Feed water	Pre-treatment	Feed spacer (thickness)
1	Spent AIX regenerate SIX® pilot	-	Standard (28 mil)
2	Spent AIX regenerate SIX® pilot	-	Thick (34 mil)
3	Spent AIX regenerate SIX® pilot	-	Thin (20 mil)
4	Spent AIX regenerate SIX® pilot	Denitrification	Standard (28 mil)
5	Spent AIX regenerate SIX® pilot	5 µm pre-filter	Standard (28 mil)
6	Spent AIX regenerate SIX® pilot	1 µm pre-filter	Standard (28 mil)
7	Spent AIX regenerate SIX® plant	-	Standard (28 mil)
8	5-7 µm Polystyrene solution	-	Standard (28 mil)

Experiment run nr. 8 includes the use of a standard particulate solution consisting of a well-defined polystyrene (PSt) particles with a narrow size distribution to be measured by particle counting. The size range was selected between 5-7 μm based on representativeness with the spent AIX regenerate stream (Figure 2) and on the commercial availability of the solution. The concentration was aimed at 15,000 particles/mL for 10 L, the solution was obtained from JP Kummer GmbH (Germany). This PSt solution is re-circulated over the flow cell while measuring the pressure drop increase and related to particle counting of the solution entering and exiting the flow cell.

3.3.4.2 Recommendations for further research with the ED particle fouling set-up

With the standard ED fouling test for particles a systematic research plan was prepared for the selection of the pre-treatment and the feed spacer using one membrane type (PCCell PCMVA anion exchange membrane). A similar research plan can be devised for membrane selection in relation to particle fouling, both for anion and cation exchange membranes selection. It is recommended to carry out this research with the same type of feed water quality (and pre-treatment) using the same feed spacer. Many ED manufacturers supply complete ED stacks consisting of given combinations of ED membranes and feed spacer type, in which particle fouling is caused by the specific ED membrane – feed spacer combination. In the ED particle fouling set-up different types of ED membranes can be investigated with the same type of feed spacers in order to focus only on the effect of the ED membrane.

Different pre-treatment systems should be compared, depending on the outcome of the planned experiments. Cartridge filters can be selected with different pore sizes, both smaller than $< 1 \mu\text{m}$ and larger than $> 5 \mu\text{m}$. Also other filtration systems can be selected such a mechanical screens, rotating drum filters, screen filters, depth filters (e.g. cartridge filters),... A very robust, but a more expensive option is using MF/UF to pre-treat the spent AIX regenerate water. MF/UF has a very high particle retention, resulting in virtually particle-free water which will eliminate feed spacer clogging based on particle fouling. This facilitates the use of very thin feed spacers, which can result in a compact ED stack design resulting in a lower energy requirement.

At the end of operation the ED membrane and feed spacers are investigated in an autopsy study to determine the extent of particle and organic fouling using SEM and AFM measurements (section 2.1.1). Additional techniques in the autopsy study can include (i) energy-dispersive X-ray spectroscopy (EDS), (ii) contact angle measurements to determine the hydrophobicity of the fouled membrane surface, (iii) Zeta-potential measurements to determine the charge of the membrane (section 2.1.1). These measurements should of course be compared to the non-fouled virgin ED membrane.

Visual observations were carried out during the particle fouling experiments, which was found to offer interesting additional information about fouling (section 3.3.3). More insight can be obtained by using high speed cameras possibly in combination with particle tracking for more detailed information about particle fouling, e.g. influence of particle size and particle deposition mechanism and information on particle-particle interaction and membrane-particle interaction.

3.4 ED membrane fouling – a discussion

For the operation of an ED desalination plant for the treatment of spent AIX regenerate, a robust and effective fouling control strategy is important. Membrane and feed spacer fouling can influence the ion transport, the rate of ion transport and permselectivity of the different anions and cations in the spent AIX regenerate stream. These properties will ultimately

contribute to the current efficiency and therefore to the power and energy requirement for such an ED process. Understanding and controlling membrane fouling is essential for the stable operation of an ED installation. Different fouling types and fouling strategies are covered in this chapter, and a rational approach is essential to determine the impact of each single fouling type and of each fouling control strategy. Different approaches can be devised dependant of fouling type and control strategy, which will determine the duration, the scale, the design and operation of the ED fouling approach. For example, for biofouling studies the duration of the experiment is typically in the order of a couple of weeks to months, opposed to particulate fouling which occurs within hours to days. To investigate scaling, the fouling approach need to be operated on realistic recovery values which require a sufficient amount of membrane area and/or re-circulation of the diluate and concentrate streams. The design and scale of a fouling experiment depends on the investigated fouling type, for example ion transport in function of organic fouling can be determined in a small lab-scale set-up, while feed spacer clogging by biofouling requires more realistic flow channels mimicking the actual flow pattern in actual ED stacks. Finally the operation of the ED fouling set-up depends on the susceptibility of ED performance parameters (e.g. ion transport and permselectivity) on ED process parameters. For example scaling is most likely influenced by the current density and should be investigated under real potential differences, while particulate fouling is mainly impacted by hydraulic conditions and can be investigated without a potential difference.

The need for an electric field during ED fouling testing depends strongly on the (expected) impact of a potential difference on the fouling type. As stated before, it is believed that this is particularly relevant in scaling, but it also might have an effect on biofouling, organic fouling and particulate fouling. Bacteria are usually negatively charged and will be transported towards the anion-exchange membrane where electrostatic attraction forces will occur resulting in an increase in biofouling. Similarly this will occur for negatively charged organic compounds which can foul and even poison the anion-exchange membrane. Positively charged organic and inorganic compounds will be transported to cation-exchange membranes where electrostatic attraction forces will occur resulting in an increase in respectively organic fouling and scaling. Particulate fouling might also be affected by an electric field, but arguably to a lesser extend as a result of relatively large dimensions of the particles. Therefore, in the presented ED particulate fouling approach it was assumed that particle transport due to a potential difference in ED is negligible. This should of course be verified experimentally.

During actual ED operation different fouling types and mechanisms will occur simultaneously and possibly results in synergistic fouling problems. The advantage of this approach is that it is realistically reflecting fouling phenomena occurring in actual ED plants and indicating the change in ED performance parameters such as ion transport (rate) and permselectivity. The disadvantage, however, is that it will be difficult to link a change in a certain ED performance indicator to a single fouling type. A systematic investigation of ED membrane fouling under actual ED operation is therefore difficult to interpret, since the impact on each operational ED parameter is not clear.

Investigation of an individual fouling type can only be done under simplified conditions or using synthetic feed water. Particulate fouling is in this report investigated at short term (hours/days) without an electric field in a single flow channel, which can also be done for biofouling at longer term (weeks/months). A single flow channel might not be representative for a total stack of membrane flow channels, which are used in ED cells. Particulate fouling will occur both at the entrance and within the different flow channels in an ED cell. Scaling can be investigated by using a synthetic solution consisting only of inorganic compounds in

the same concentration as in actual spent AIX regenerate streams. The advantage of this approach is a better understanding of the impact of each fouling type on the ED performance parameters. The disadvantage is that many assumptions have to be made which might render the results not completely representative. Furthermore, it is impossible to assess the effects of synergistic fouling effects.

4 ED design

The full-scale ED plant for treatment of spent AIX regenerate has two goals: (i) maximum recovery of sodium chloride salt in the first stage and (ii) maximum purification of the NOM flow in the second stage. One stage ED design focuses on salt recovery, while two stage ED design also aims at NOM stream purification. In this chapter an ED design procedure was suggested to determine the optimal set point of an ED installation depending on ED membrane and installation costs. At the end of the chapter these recommendations are related to a practical design approach by Eurodia, which was not disclosed.

4.1 ED design procedure

4.1.1 Background

In this section a design procedure for ED design is presented based on an experimental procedure (KOA98.050, KOA98.165 and Cowan and Brown, 1959). On the basis of this design procedure parameters are determined which are necessary to determine the membrane and energy cost of an ED plant. In 1996-2000 a series of studies were conducted in the Netherlands to acquire design parameters for ED plants for the removal of nitrate, hardness, sulphate and carbonate from groundwater using ED. These studies were conducted by WML (Waterleiding Maatschappij Limburg), WOB (Waterleidingmaatschappij Oost Brabant, now Brabant Water), VMW (Vlaamse Maatschappij voor Watervoorziening, now De Watergroep) and Kiwa Onderzoek en Advies (now KWR). The approach was aimed at acquiring an ED plant design by conducting a limited set of experiments and measurements in function of a given feed water quality and a desired product water quality. The optimal operational set point of the ED plant depends on the ED membrane and installation cost.

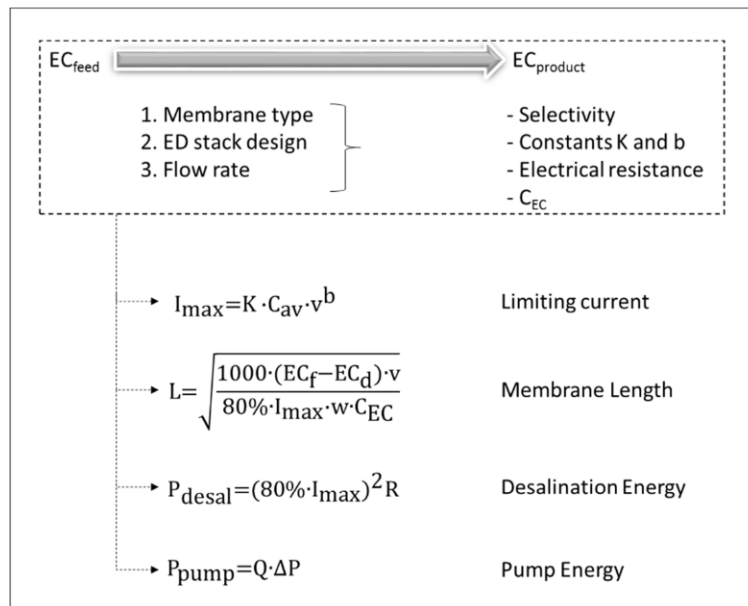
4.1.2 A brief explanation of the ED design procedure

The goal of ED is to reach a desired water quality, which depends on the selectivity of the membrane and is expressed as the TDS removed or conductivity removed. Ideally, this should be reached with a minimum energy input and a minimum membrane area at a maximum recovery value of the ED plant. The variables which influence the ED design and operation are: (i) membrane type, (ii) ED stack design (hydraulic conditions) and (iii) flow rate. For each selection/setting of these variables the optimal (maximum) or limiting current density I_{\max} should be assessed. For each setting the hydraulic resistance (pumping energy) and electrical resistance (desalination energy) will be determined. After this the required membrane length and membrane area can be calculated (see Figure 4.1).

The number of required experiments to determine the ED design criteria to optimize investment cost, energy cost or recovery can be substantially reduced with the proposed method. For each membrane type and ED stack design, I_{\max} should be determined at different (minimal six) flow rates together with measurement of the product water quality and determination of the hydraulic and electric resistance.

From the results of the experimental procedure together with cost information from ED suppliers, the optimal set point for ED operation can be determined. After this it is important to carry out long term pilot experiments to provide information on membrane fouling and cleaning.

FIGURE 4.1 SCHEMATIC OVERVIEW OF THE ED DESIGN PROCEDURE



In Figure 4.1 I_{max} is the optimal (maximum) or limiting current density (mA/cm^2), C_{av} is the average product concentration (meq/cm^3), K is an empirical constant depending on the spacer type, distance between the membranes and temperature (between 50 and 200), b is an empirical constant depending on the membrane type (between 0.5 and 0.9), v is the flow rate (m/s), L is the membrane length (m), w is the membrane width (m) and R is the total stack resistance ($\Omega \cdot \text{cm}^2$).

4.1.2.1 Method for determining the limiting current I_{max}

As a result of concentration polarization in ED, (i) the salt concentration at the membrane surface in the diluate chamber decreases and (ii) the salt concentration at the membrane surface in the concentrate chamber increases. When the salt concentration at the membrane surface at the concentrate side exceeds the solubility limits, scaling will occur which will result in an additional electrical resistance (see chapter 3). When the salt concentration at the membrane surface at the diluate side reduces to zero there are no more ions available for ion transport and the voltage will sharply increase resulting in a high energy consumption during ED (Strathmann, 2004). Therefore concentration polarization effects should be minimized during practical ED operation. This is possible by reducing the current density or by improving the hydraulic conditions in the ED cell (increasing flow rate, cell design, spacer type, etc.). If the hydraulic conditions remain constant only the current density can be limiting. The maximum current density is reached when the salt concentration (at the membrane surface in the diluate chamber) becomes zero. This current density is referred to as the limiting current density. In the proposed ED design procedure, the limiting current should be determined at six flow rates for each membrane type and ED stack design.

- After calibrating the conductivity and pH meters, the diluate and concentrate (e.g. $\frac{1}{2} Q_{\text{dil}}$ for 50% recovery) flows through the ED set-up should be set.
- Make sure that the pressure at the diluate side is 0.1 bar higher than at the concentrate side and that air is removed from the equipment and tubes.
- Stabilize the installation for 3-5 minutes at the first current setting (not too close to the expected limiting current), and measure the pH and conductivity of the feed, diluate and

concentrate streams. Also measure the voltage and current from the data logger to calculate the resistance.

- Increase the current stepwise to the next settings and repeat the procedure (measure pH, conductivity, current and voltage).
- Plot the resistance (V/I) against the reciprocal current (I) and determine the limiting current I_{\max} , which is at the minimum resistance value in the plot (see figure 4.2).
- When the limiting current I_{\max} is determined at a certain flow rate the ED is run at 80% I_{\max} and stabilized during 30 minutes of operation.
- During this operation feed, diluate and concentrate samples are taken for further analysis of the ionic composition and DOC level of the streams. The ED removal capacity for these parameters can be determined from these results.

FIGURE 4.2 GRAPHICAL DETERMINATION OF I_{\max} FOR TWO DIFFERENT FLOW RATES

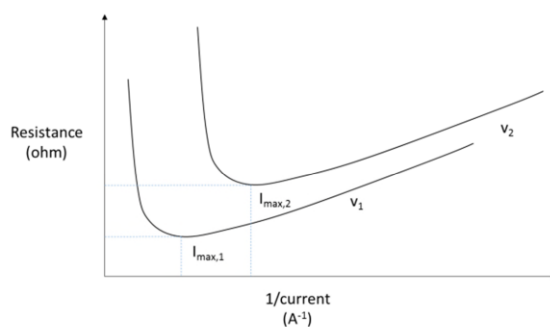
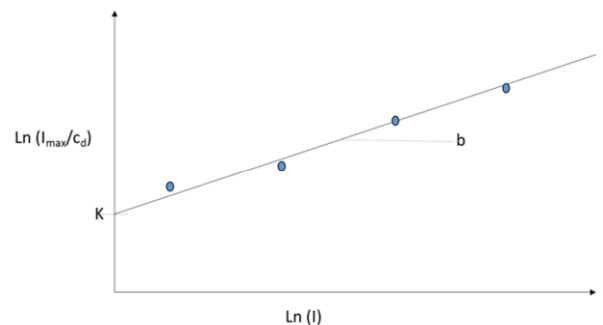


FIGURE 4.3 CORRELATION BETWEEN THE TWO STACK CONSTANTS B AND K



4.1.2.2 Method for determining the stack constants K and b

For each ED membrane type and ED stack design the stack constants K and b need to be determined.

- Determine the limiting current I_{\max} at different flow rates over a certain stack (6 points).
- Plot the natural logarithm of I_{\max} over the product/diluate concentration c_d versus the natural logarithm of the flow rate as $\left(\text{Ln}\left(\frac{I_{\max}}{c_d}\right) = \text{Ln} K + b \cdot \text{Ln} v\right)$ and determine K and b by a linear curve fitting (see figure 4.3).
- K (intersection with y-axis) depends on the spacer type, the distance between the membranes and temperature (between 50-200).
- b (slope of the line) depends on the membrane type (between 0.5-0.9).

4.1.2.3 Determine c_{EC}

- During the limiting current determination method, the feed and diluate conductivity is registered at each current setting.
- A linear correlation exists between the reduction in the conductivity ($\Delta\text{EC} = \text{EC}_f - \text{EC}_d$) and the applied current. The slope of the curve depends on the flow rate; at low flow rates the slope is smaller.
- Calculate C_{EC} from the average $\Delta\text{EC}/\ell$ values at different flow rates divided by the retention time in the stack.
- C_{EC} is approximately the same at every flow rate, and gives the value for a given ED membrane type and stack.

4.1.3 Validation of the experiments

After determining K , b and C_{EC} for a certain stack using the stepwise current increase method to determine I_{max} , the results will be translated to practical ED operation.

- Calculate the required flow rate (v) and electrical current from:

$$I_{max} = K \cdot C_{av} \cdot v^b$$

$$L = \sqrt{\frac{1000 \cdot (EC_f - EC_d) \cdot v}{80\% \cdot I_{max} \cdot w \cdot C_{EC}}}$$

- The membrane length is set beforehand based on the actual information of the ED supplier. Furthermore the concentration of the feed and diluate solution is set to the actual conditions (aiming for approx. 50% removal).
- Adjust the ED pilot to the calculated flow rate and I_{max} and stabilize the set-up during 30 minutes.
- After stabilization verify the diluate conductivity and verify if the removal efficiency is achieved. If not, adjust the electrical current to meet the desired removal efficiency.
- When the pilot is stabilized and set on the correct conductivity, samples can be taken and analyzed to determine the required parameters (both for removal and scaling calculations).

4.1.4 Effect of ED membrane ageing on design

The effect of ED membrane ageing is one of the most challenging and unknown issues during the design of ED plants. Most probably the effect of ageing and the coupled lifetime expectancy is known to ED suppliers based on their operational and practical experience. Ageing and lifetime expectancy is strongly related to the type of feed water, and in the case of an unknown feed water type, such as spent AIX regenerate streams, knowledge on membrane ageing is limited.

In case of the design of reverse osmosis (RO) installations typically publicly available software tools are available developed by different RO membrane suppliers. In some of the RO design software tools membrane lifetime can be simulated by a loss in salt passage, typically 5-10% per year depending on the feed water type. For ED installations, publicly available software tools are not available (probably because of a smaller market share of ED membranes compared to RO membranes). In analogy with RO, however, an increase in permselectivity might be assumed of 5-10% per year. This is an educated guess and should be validated in practice.

4.1.5 Recommended ED design procedure in relation to practical design considerations

PWNT intends to use ED for the treatment of spent AIX regenerate streams (section 1.1). First a pilot approach is foreseen followed by a demonstration plant using ED to treat spent AIX regenerate. The question is how the recommended design procedure presented in this chapter relates to the design of the pilot installation and demo plant. The presented ED design approach was taken from literature, and was reported in some older KWR-reports based on ED research in drinking water treatment, more specifically used to remove nitrate from groundwater. It was used to calculate the expected cost of ED installation at an optimal design.

PWNT has contracted in the runtime of this project the ED membrane and system supplier Eurodia who have many years of experience on the design and construction of ED plants in practice (<http://www.eurodia.com/index.php/en/>). Eurodia seems to design ED installations

via a different methodology. Eurodia have a portfolio of ED membranes which they work with and design ED installations according to their own standard applications, which consists predominantly of ED applications in dairy & cheese production, wine making and sugar and starch industries. Eurodia states that ED membranes are always operated at a maximum voltage and pilot testing is done to establish (i) the salt /ion transfer and (iii) desired recovery. Based on these parameters an installation is designed. The exact ED design procedure is not fully disclosed by Eurodia, and therefore it is not possible to make a comparison between the recommended ED design procedure in this chapter and the practical ED design procedure by Eurodia. Operation at a maximum voltage is not the most energy efficient operation, but is probably done by Eurodia to minimize the membrane area which is currently still the most expensive part of an ED installation because of a relatively high ED membrane cost.

Both ED design procedures were developed for a different ED application, in the case of the recommended ED design procedure in this chapter it was nitrate removal from groundwater and in the case of Eurodia it was for application in food industry. It is likely that ED application for treating spent AIX regenerates requires a specific and different approach.

5 Conclusions and recommendations

This report provide supporting protocols for (i) ED membrane selection, (ii) ED fouling and (iii) ED design divided into three main chapters. The conclusion and recommendations of these chapters are summed up below.

5.1 Conclusions

5.1.1 ED Membrane Selection

- A proper membrane selection is essential for the design of an ED installation.
- Membrane selection is based on (i) ED membrane characterization and on (ii) ED process performance comparison.
- ED membrane characterization is based on determination of material properties (e.g. mechanical stability, membrane thickness, swelling degree and water permeability) and electrochemical properties (e.g. ion-exchange capacity, membrane resistance and permselectivity).
- Best available ED membranes are expected to have a high ion-exchange capacity (and therefore high swelling degree), a low membrane resistance and a high permselectivity for the relevant anions and/or cations. Water permeability should be low and thickness coupled to mechanical stability should be sufficient.
- Characterization data is easily accessible, independent of ED application, available for a single ED membrane, but is usually incomplete (or lacking), dependent on applied methods and time-consuming to obtain.
- ED process performance parameters include (rate of) ion transport, specific permselectivity, current utilization and power & energy requirement.
- The most efficient ED membrane(s) (pairs) should display a high ion transport (rate), a high transport number, a high specific permselectivity (e.g. chloride relative to sulphates) and a high current utilization which translate into a low power and energy requirement.
- Performance parameter data is specific and includes practical issues (e.g. fouling), but is limited to specific circumstances, limited in gaining understanding and only provides ED membrane info in pairs.
- The feed water type is important for membrane selection, which determines the efficiency of ion transport and fouling of the membrane. In this report spent AIX regenerate was used from Andijk III (PWN).
- A practical approach was suggested using an IEC/PCCell laboratory ED set-up for membrane performance for testing at the PWN pilot facilities in Andijk.
- The effect of NOM on the ED performance was found to be important, and for an ED testing protocol the effect of the presence of NOM should be evaluated.

5.1.2 ED Membrane Fouling and Ageing

- Fouling during ED processes can result in a decrease of the diluate flow (due to clogging of the feed spacer), an increase of the electrical resistance, a permselectivity decrease and a membrane modification.
- ED membrane fouling is a complex phenomenon involving different fouling types (particulate fouling, biofouling, organic fouling and scaling) which occur simultaneously when operating an ED installation using actual feed water.
- Control of ED fouling can be subdivided into (i) pre-treatment, (ii) feed water conditioning, (iii) ED membrane selection, (iv) process control and (v) chemical cleaning.
- Particulate fouling appeared to be a dominant fouling mechanism during ED on raw spent anion exchange regenerate at PWNT in Andijk.
- A systematic ED fouling approach was proposed to relate the presence of particulate material in feed water to a hydrodynamic pressure loss increase at constant feed flow in a representative flow cell mimicking flow channels in an actual ED stack.
- A change in particle size distribution after passing the flow cell was related to an increase in pressure drop, which was attributed to entrapment/precipitation of particles in the flow channel corroborated with visual observations.
- As a result of regular chemical cleaning, ED membranes will age resulting in the loss of ion exchange capacity.
- Regular acid–base cleaning cycles resulted in membrane inflate–deflate sequences causing cracks and fractures in the structure leading to membrane toughness deterioration.
- A systematic research plan was devised focusing on selection of the (i) pre-treatment system, (ii) feed spacer configuration and (3) ED membrane type (in relation to fouling and ageing).
- A validation experiment is planned with the ED fouling approach using a standard particulate solution consisting of well-defined polystyrene (PSt) particles.

5.1.3 ED Membrane Design

- An ED design approach was suggested aimed at acquiring an ED plant design by conducting a limited set of experiments and measurements in function of a given feed water quality and a desired product water quality. The optimal operational set point of the ED plant depends on the ED membrane and installation cost.
- The variables which influence the ED design and operation are: (i) membrane type, (ii) ED stack design (hydraulic conditions) and (iii) flow rate. For each selection/setting of these variables the optimal (maximum) or limiting current density I_{\max} should be assessed.
- From the results of the experimental procedure together with cost information from ED suppliers, the optimal set point for ED operation can be determined.
- Eurodia designs ED installations via a different non-disclosed methodology using selected ED membranes according to their own standard applications, which cannot be compared to the suggested ED design method.

5.2 Recommendations

5.2.1 ED Membrane Selection

An ED testing protocol should contain both ED membrane characterization and ED performance comparison for ED membrane selection. A pre-selection of different ED membranes can be made on the basis of available ED characterization data, while in the next phase pre-selected ED membranes should be experimentally compared in an ED performance

comparison study. To gain a more fundamental understanding, ED membranes can be characterized using standard set-ups and methods before and after ED application, more specifically by (i) determining AFM, SEM, EDS, zeta potential and contact angles (2.1.1) and (ii) ion-exchange capacity by titration, determining the electrical membrane resistance and permselectivity in a standard ED cell (2.1.2). It is expected that fouled ED membranes will display different characterization parameters. The effect of NOM in spent AIX regenerate on the ED performance should be studied systematically (2.4), e.g. by taking and storing a large sample of actual spent AIX regenerate and treat this as a standard solution. This can be compared to the ED performance using a synthetic spent AIX regenerate only containing the salts. A practical approach is suggested using an IEC/PCCell laboratory ED set-up for membrane performance for testing at the PWN pilot facilities in Andijk. Furthermore, a six compartment ED set-up is suggested for a more thorough ED membrane characterization at the UT or Wetsus.

5.2.2 ED Membrane Fouling and Ageing

The standard ED fouling approach was developed for the selection of pre-treatment and feed spacer type, but can also be used for ED membrane selection in relation to fouling. Visual observation can be enhanced by combination of high speed cameras, and the ED membrane and feed spacer after the ED experiment can be extensively studied using high-tech material characterization techniques. Fouling types can be studied with the standard ED fouling approach for fouling types, e.g. particulate fouling which are relatively unaffected by the omission of an electric field. In all other cases the effect of fouling (e.g. biofouling and scaling) on ED performance should be investigated in an actual ED set-up using an electric field. Furthermore, studying synergistic effects of different ED fouling types should be investigated in actual ED set-ups, particularly organic fouling in combination with biofouling is of interest.

Membrane ageing results in the loss of ion exchange capacity and mechanical strength. Membrane ageing has an expected important impact on ED design, which is not reported in literature and possibly known by ED manufacturer from practical experience. It is suggested to use a factor of an assumed 5-10% yearly permselectivity loss in analogy with RO design. Membrane ageing should be studied on a longer scale experiments (months to years) focusing on the change in electrochemical properties (ion transport rate, permselectivity and current utilization).

5.2.3 ED Membrane Design

The proposed ED design procedure and/or the Eurodia design procedure should be used for mono-selective ED membranes on spent AIX regenerate after SIX® and for non-selective ED membranes on spent AIX regenerate after SIX® and mono-selective ED membrane treatment. This in order to estimate the membrane cost and desalination and pumping energy cost of the ED installation. After this it is important to carry out long term pilot experiments to provide information on membrane fouling and cleaning, which is one of the activities in the PhD project of Elisabeth Vaudevire.

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Appendix I Particle Counter (Pamas)

The particle counter (pc) used for these experiments is from Pamas, type WaterViewer. This pc has eight channels allowing counting the particles between 1 to 100 μm . One is able to choose the range of each channel. The chosen channel depends on the experiment and the expected composition of particles. The flow used is about 25 mL/min. The chosen sampling time is 2 minutes. After every 2 minutes the particle counter gives an average number of particles for each channel measured in 50 ml of water expressed as particles per ml. The particle counter is linked to a computer with Pamas WaterViewer software.

The particle counter is equipped with a pump. This pump delivers a constant flow of 25 mL/min to the detector. The detector consists of a transmitter and a receiver. The water sample flows between this transmitter and receiver. If there are particles in the water they will partially block the laser beam which is sent to the receiver. The receiver measures a difference in current. These current is linked to a specific particle size by a calibration curve performed by Pamas. By measuring the current on the receiver, the number and size of the particles are calculated.

The pump of Pamas particle counter sucks the water in normal and reverse ways. To avoid the damage of particles the pump needs to be put after the measurement cell. During this study, all the experiments presented in this report are performed in the reverse mode (pump after the measurement cell).

FIGURE 1 PHOTO OF THE PAMAS WATERVIEWER PARTICLE COUNTER



Appendix II ED design procedure

Example of calculation routine

Calculation costs (@ known A_m and v) (KOA 98.050)			
Calculated:	Emile Cornelissen		
Date:	16-4-2015		
Pilot and full-scale data		Cost variables	
v	15,0 [cm/s]	kWh cost	€ 0,15
membrane width (pilot)	10,0 [cm]	Membrane cost	€ 250 /m ²
Thickness spacer	0,5 [mm]	Depreciation	5 year
Voltage per cel	0,5 [V]	Peak factor	1,5
Efficiency	0,7 [%]	Hours	8760 hrs/year
Experimentally determined parameters			
K	42,19	PAS OP: PILOT vs FULL-SCALE WIDTH ?	
b	0,77		
EC_{feed}	0,00700 [meq/cm ³]		
$EC_{product}$	0,00390 [meq/cm ³]		
C_{EGV}	20,64 [μ S/cm/A/s]		
Safety factor	0,8 [% I of I_{max}]		
Calculated values			
Q_f	0,027 [m ³ /cell]	Feed Flow	
Number of cells	37,0 [cell/m ³]	Number of cells	
L	125,1 [cm]	Length membrane	
I_{max}	1,80 [mA/cm ²]	Limited current density	
80% I_{max}	1,44 [mA/cm ²]		
I	1,80 [A]	Actual supplied	
A_m	9,27 [m ² /m ³]	Membrane area	
C_d	0,00530 [meq/cm ³]	Average concentration product	
Calculation costs			
Membrane Cost	€ 0,079 [€/m ³]		
Desal Energy Cost	€ 0,007 [€/m ³]	47,64 [kWh/m ³]	
Pumping Energy Cost	€ 0,039 [€/m ³]	56,8 kPa	
		4 Nr. pumps	
Total Cost	€ 0,125		